HEXAFLUOROTANTALATE(V)-SELECTIVE LIQUID MEMBRANE ELECTRODE BASED ON BRILLIANT GREEN

BY
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TO MY FATHER, WHO LEFT SUDDENLY,

AND MY MOTHER

AND

TO THE PARENTS OF ENGDAWORK ZEWDIE

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ABSTRACT

HEXAFLUOROTANTALATE(V)-SELECTIVE LIQUID MEMBRANE ELECTRODE BASED ON BRILLIANT GREEN

BY

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Research Advisor; Dr B.S. Chandravanshi

Brilliant Green-hexafluorotantalate(V) extract in nitrobenzene was used to prepare hexafluorotantalate(V) liquid membrane electrode with a PVC support. The electrode body was made from the concentric polypropylene tubes (16.5 cm long with internal diameter of the outer and inner tubes, 8 mm and 4 mm, respectively) which were joined by a cork. The liquid membrane electrode was connected with fluoride-selective electrode as internal reference and ground glass diaphragm (Ag/AgCl) electrode as external reference electrode, to obtain the complete cell assembly for the potential measurements. The concentrations of sulphuric and hydrofluoric acids, for the optimum response of the electrode to hexafluorotantalate(V) were found to be 1.0 M in the test solutions. The response characteristics of the electrode have been evaluated, and the electrode was found to respond to hexafluorotantalate(V) in the concentration range of 2.0×10^{-6} - 1.0×10^{-2} M tantalum(V) with a sub-Nernstian slope and detection limit of -58.5 mV/decade and 3.69×10^{-7} M tantalum(V), respectively.

The effects of forty diverse ions on the electrode response to the hexafluorotantalate(V) abion have been studied to evaluate the selectivity of the electrode. The newly developed liquid membrane electrode has been applied successfully to the determination of tantalum in tantalite-columbite ores by direct potentiometry, standard addition and sample addition, and Gran's plot potentiometric techniques.

1. INTRODUCTION

1.1. Occurrence and Uses of Tantalum

Tantalum, symbol Ta, is a chemical element of atomic number 73 and atomic weight 180.95. It is a member of the fifth group of the periodic table, and is in the 5d transition series. It's valence electronic configuration is 5d3 6S2 , which accounts for its maximum oxidation state of +5[1-3].

The metal, tantalum, does not occur naturally in the free state. It is found in a number of oxide minerals which almost invariably contain niobium also. In terms of abundance, tantalum does not appear on the list of the first 65 elements that are found in the seawater. It does not also appear on the list of the first 36 elements that occur in the earth's crust, and hence relatively scarce. The element occurs in the earth's crust to the extent of 2.1 X 10-4 %[1-4].

The most tantalum bearing minerals are tantalite and columbite which are variations of the same natural compound, (Fe,Mn)(Ta,Nb)2O6. Tantalite-columbite occurs in some pegmatite in quantities which seldom exceed a few pounds per ton and in alluvium derived from such pegmatites. Other tantalum minerals except microlite, (Na,Ca)2Ta2O6(O,OH,F), have little significance as a source of tantalum. These are manganotantalite,

Mn(Ta,Nb)206, tapiolite, Fe(Ta,Nb)206, skogbolite, FeTa206, simpsonite or calogerasite, Al2Ta208 + CaO as an impurity, thoreaulite, SnTa207 + CaO and Nb205 as impurities, stibiotantalite, (Sb,Bi)(Ta,Nb)04, yttrotantalite, (Fe,Ca)2 (Y,Er,Ce,U)2(Ta-,Nb)4015 + 4 H20, euxenite, (Y,Ca,Ce,U,Th) (Ta,Nb,Ti)206, and tanteuxonite, (Y,Er,Ce,U)(Ta,Nb)(Ti)06.[1,3-6].

Tantalum is best known as a refractory metal with a combination of unique properties making it useful in a great variety of commercial applicatins, though its applications are inhibited somewhat by its relatively high cost. It is used widely, although in small quantities, in the manufacture of capacitors for electronic equipment including band radios, heart pacemakers, emitters, getters, and automobiles2. The extreme corrosion resistance of tantalum at normal temperatures (due to the presence of exceptionally tenacious film of oxide) leads to its application in the construction of chemical plant, especially where it can be used as a liner inside cheaper metals. The corrosion resistance of tantalum has been compared with that of glass. Additionally, the metal has a high heat transfer coefficient, and is easy to fabricate. Consequently, it finds use in equipment that must resist strong corrosive attack, as in the manufacture of HCl, hydrogen peroxide, in chromium plating baths, in bromine heaters and stills, and in the preparation of corrosive fine chemicals. The metal has also been used in resistance heaters in very high temperature furnace and for some nuclear reactor parts7-9.

Moreover, tantalum has got several important surgical and

dental applications because of the inertness of the metal to body fluids and the tolerance of the body for the metal. It may be placed in the skull, or other body parts without rejection. Strips and screws made of tantalum are used for holding broken pieces of bone, and the wire mesh is used for surgical staples, braid for sutures, and reinforcements[2,3,6].

Tantalum is also added to nickel and nickel-cobalt super-alloys for gas-turbine and jet engine parts. Tantalum-base alloys are used for aerospace structures and space power systems, principally because of the high temperature stability and strength of these alloys[6].

A tantalum-tungsten alloy is used for fabricating spring for high temperature at high vacuum applications. The tensile strength of ternary alloys of tantalum (tantalum with 30 % niobium and 5 % zirconium or vanadium) at room temperature is about three times that of tantalum alone, and the alloy finds several uses in industry and aerospace structures. Other metals such as hafnium, molybdenum, rhenium are also added to tatalum, though in small amount, to give significant tensile strengh.

The ferrotantalum, which is added to austentitic steels to reduce the intergranular corrosion, has also many uses in several related areas.

1.2. General Properties and Chemistry of Tantalum[4-11]

Tantalum is a slightly bluish metal, ductite, maleable, and when polished resembles platinum. Elemental tantalum has a

body-centered cubic crystal structure. It has a melting point of 2,996oC, boiling point of 5,427oC, and density of 16.68 g/cm3 (solid at 20oC), and 17.1 g/cm3 (single crystal). Because of its high melting point, it is considered a refractory metal6.

The metal is quite inert to acidic attack except hydrofluoric acid and fuming sulphuric acid. It also dissolves in molten alkalis, concentrated alkaline solutions and fluoride in acid media. It is very resistant to attack by liquid metals such as lithium, sodium, potassium, sodium-potassium alloy, lead, mercury and gallium provided these liquid metals contain no oxygen4.

There is a strong similarity between the chemistries of tantalum and niobium, which is significantly different from that of their group congener, vanadium4. As a consequence of the lanthanide contraction their atomic (1.47 Ao) and ionic (0.69 Ao) (for + 5 oxidation state) radii are identical, which are appreciably larger than the corresponding values for vanadium, 1.34 Ao and 0.59 Ao, respectively. One consequence of the size difference is that the lower oxidation state of both metals, tantalum and niobium, are of relatively minor importance. Thus, apart from the halide chemistry, the vast majority of character-ized compounds of the matals are pentavalent, although compounds with formal oxidation states of +4,+3,+2,+1,0 and -1 have been reported, these oxidation states, in particular the first three, are less well characterized. In contrast to vanadium, for which the species VO+ and , particlarly VO+2 play important roles, tantalum and niobium have virtually no cation chemistry. Their oxides,

Ta_2O_5, and Nb_2O_5, are appreciably basic, while that of vanadium, V_2O_5, is amphoteric. There is also considerable similarity in the chemistry of lower halides, of tantalum and niobium, where metal-metal bonding is important, and in their numerous integral valence stable cluster compounds.

Differences are also observed, though not profound, between the chemistries of tantalum and niobium4. For example, it is well established that tantalum(V) is less readily reduced than niobium(V), and is more readily hydrolysed in aqueous hydrochloric acid solutions. In addition, there are differences in the structural chemistry of the respective peroxides, in the stability of the pentavalent oxyhalides, and the nature of oxysulphates obtained from aqueous solutions.

The pentoxide,Ta_2O_5,can be obtained by heating the metal in oxygen or by dehydration of the hydrated oxide. The pentoxide is white, air stable, and water-insoluble solid which is an important starting material for tantalum production. The pentoxide is hardly attacked by mineral acids, with the exception of hydrofluoric acid. It can be melted by fusion with alkali metal pyrosulphates, potassium hydroxide or carbonate, the mixture of potassium carbonate and potassium nitrate; and the resulting melt may be dissolved in acidic solution or, depending on its composition, in water4.

Besides the pentoxide, other oxides of compostions TaO_x ($x<2.5$) are in evidence in the oxidation state of tantalum metal with oxygen, though no discrete TaO and TaO_2 compounds are known12. They are formed by active metal reduction. TaO_2 forms,

with alkali metals, the metatantalates, MTaO3, the orthotantalates, M3TaO4, and pyrotantalates, M4Ta2O7, as well as the polytantalates of compostion M8Ta6O19 which require fusion with alkali hydroxides6.

Tantalates are obtained by fusing the pentoxide with alkali hydroxides or carbonates, which hydrolyse to oxide upon washing with water. The melt can be extracted in the aqueous potassium hydroxide, and upon treating it with ethanol, a product of composition K8Ta6O19.16H2O precipitates. The anion, Ta6O19^{8-}, also exists in aqueous solution in the pH range of 10-13, without being subjected to further polymerization, depolymerization or protonation. Upon acidification, the hydrous oxide precipitates. Although it is called tantalic acid, it is insoluble in aqueous bases, but soluble in acid, and salts of composition KTaF6, K2TaF7, and K3TaF8 can be crystallized from aqueous solutions of different fluoride concentrations1-3.

In aqueous fluoride media there exists a distribution of a series of fluorotantalate complexes of composition Tav Fn^{5-n} (n < 8)4. Equilibrium of the formation of various complexes depends on many factors: viz, concentration of the free fluoride ion, concentration of tantalum, and also the acidity of the medium. Predominant species in specific solutions, as deduced from Raman and n.m.r. spectra, are [TaF6]$^{-}$(24 M HF, no [TaF7]$^{2-}$ [TaF7]$^{2-}$ (5.2 M NH4F, no [TaF6]$^{-}$), and [TaF6]$^{-}$ and [TaF7]$^{2-}$ (8.1-11.0 M HF), with the formation constants of 4.6 x 10^{3}, 1.26 x 10^{3} and 4.5 for [TaF6]$^{-}$, [TaF7]$^{2-}$ and [TaF8]$^{3-}$, respectively4. The [TaF8]$^{3-}$ anion has not been detected by Raman technique in

hydrofluoric acid solutions up to 24 M. There is a conflicting evidence for the existence of [TaF9]4- in aqueous fluoride media and no solid complexes containing this anion have yet been prepared. The preparation of the fully halogenated (i.e., non-oxygenated) compounds requires the use of non-aqueous solvents4.

1.8. Methods of Determination of Tantalum

A large number of instrumental as well as chemical methods have been reported, in the literature, for the determination of tantalum in ores and various natural samples. Only few of the most commonly used ones are described below.

Tantalum is determined, most frequently, by spectrophotometric methods using a variety of reagents. Pyrogallol is, perhaps, one of such reagents13. It reacts with tantalum(V) in a medium of 4 N HCl and 0.0175 M $H_2C_2O_4$ to form a soluble complex compound. The molar extinction coefficient of the complex solution is 4.8 × 103 M^{-1} cm^{-1} at 325 nm. The Beer's law holds for tantalum concentration to 40 µg/ml. Mo(VI), W(VI), U(VI), and Sn(IV) interfere with the determination. The effect of Nb(V), Ti(IV), Cr(III), V(V), Bi and Cu is insignificant and can be compensated by adding these ions into the blank solution. Platinum and fluoride ions interfer with the determination of tantalum. Thus, platinum crucible should not be used to fuse the sample if the metal is to be determined by pyrogallol.

Gravimetric method of analysis generally involves precipitation of the metal ion with a suitable reagent followed by ignition of the precipitate to the pentoxide. Benzohydroxamic

acid derivatives14,15 quantitatively precipitate tantalum from the aqueous solution of pH 0.5-1.8. These reagents are also employed for separation of tantalum from niobium by selecting the appropriate pH range (3.5-6.5 for Nb, and 0.5-1.8 for Ta). The interference of Ti(IV) and Zr(IV) can be eliminated by masking with fluoride and EDTA, respectively. However, Mo(VI) and W(VI) interfere seriously. The method is fairly selective, but tedious, less sensitive and not effective for determination of small quantity of the element.

Titrimetric methods have not widely been applied for determination of tantalum because +5 oxidation state of the metal is the only stable state. However, an indirect titrimetric methods have been reported16,17. These methods involve the titrimetric application of outer-sphere complex formation of the anionic fluoro-complex of tantalum(V) in aqueous dimethyl sulphoxide. Heptafluorotantalate(V) form soluble outer-sphere complex with potassium ion in a medium of aqueous 90 % (v/v) dimethyl sulphoxide. Such complex formation can be used for spectrophotometric titration of microgram amount of tantalum with 1 to 100 mM KCl at 626 nm using nitrosulphonazo(III)16, and nitchroazo17 as indicators. In practical analysis, the method is not very common since compounds of tantalum(V) are not reduced in aqueous solutions18.

Atomic-absorption spectroscopic method for determination of tantalum(V), in industrial raw materials18 and intermediates such as niobates and tantalates19, has been used at 271.5 nm in a nitrogen-separated nitrous oxide-acetylene flame. However, the

method is subjected to strong interferences and has poor limit of detection.

The determination of tantalum by potentiometric titration technique has been done in non-aqueous media. Tantalum(V) reacts with 3-aminopyrazinoic acid to form a 1:1 complex20. The metal, in dimethyl formamide, was determined by direct and reverse potentiometric titration with 0.01 M of the reagent in the solvent. However, interference from some ions such as niobium(V) titanium(IV), iron(III) and tungsten(VI) was noted, and the method is not favourable for determination of small quantity of tantalum. Potentiometric titration of tanttalum(V) with bis (quinolin-8-ol) has also been reported21.

Ion-selective electrodes for determination of tantalum have been developed recently based on cetylpyridinium chloride-hexafluorotantalate(V)22, which was applied in potentiometric titration23, and tetraoctylammonium-hexafluorotantalate(V)24 liquid memberanes responding to hexafluorotantalate(V). The application of the former electrode has been extended to the determination of tantalum in niobium25, and in steel samples26. However, this electrode suffers from interferences of several ions such as Nb(V), Ni(II), Fe(III), Al(III), and Ti(IV). Moreover, the electrode responded to a linear function of hexafluorotantalate(V) in the concentration range of only 10-5-10-4 M. The latter electrode, i.e., electrode with tetraoctylammonium active material, has a better range of response; 2.0 × 10-6-1.0 × 10-2 M, but the application of this electrode has never appeared in the literature. In addition, the selectivity study

has been performed only for few ions such as Cl-, NO3-, HSO4, NbOF52-, and ClO4- ions.

A general anion-selective PVC membrane electrode based on tetradodecylammonium iodide27 was prepared and it was observed to respond to twenty anions, one of which is hexafluorotantalate-(V). The electrode has also been used as an indicator electrode in potentiometric titrations and catalytic potentiometric determinations concerning the twenty anions. The authors claimed that the study of general electrode further confirms that the mechanism of ion-association type ion-selective electrodes is a nonspecific ion-selective electrode.

Triheptyldodecylammonium iodide was found to be useful as the active material for ion-selective electrodes28. It was prepared by reacting 94 g triheptylamine with 100 g dodecyl iodide in 150 ml ethanol under reflux for 64 h. This active material was used for tetrafluoroborate(III), picrate, and hexafluorotantalate(V) anion-selective membrane electrodes. The linear detection range and detection limit, respectively, were 10-6-10-1 M and 8.0x10-7 M for tetrafluoroborate(III), 10-6-10-2 M and 5.0 x 10-7 M for picrate, and 10-6-10-1 M and no data for detection limit for hexafluorotantalate(V). There is no report of any slectivity study and application of the electrode.

A radiotracer studies with 182Ta showed that PVC matrix membranes containing a liquid ion-exchanger based on triheptyldo-decylammonium-hexafluorotantalate(V) sensor plus bis (ethylhexyl) phthalate mediator are permselective to hexafluorotantalate(V)29. The information available for selectivity is only for ClO4-, NO2-

Br-, and Cl- ions. Moreover, the characterstics of the electrode was not tested with either real or artificial samples.

Aforegoing discussion reveals that few ion-selective electrodes were developed for hexafluorotantalate(V) during the last ten years, and the studies of the behavior of the electrodes; such as selectivity, application, and stability are insufficiently well. Thus the development of a new type of ion-selective electrode from cheaper materials which is fairly precise, simple and sensitive is reasonable for quantification of tantalum in all artificial, intermediate and ore samples.

1.4. Aim and Scope of the Present Investigation

The triphenylmethane dyes, such as Brilliant Green, Crystal Violet, etc., are a monovalent cationic species forming ion-pairs with anions, having a number of desirable properties to be extracted into water immiscible solvents. These cationic dyes were used as ion-exchangers in electrodes selective to different organic and inorganic anions including tertrathioyanatozinczte(-II)30, perchlorate 31,32, tetrafluoroborate33, salicylate34 , phthalate35 , detergent anions36 , and tetrachloroferrate(III)37.

Brilliant Green-hexafluorotantalate(V) ion-association complex has been employed for extraction-spectrophotometric determination of tantalum38. However, there no any report in the literature the possible application of Brilliant Green-hexafluorotantalate(V) ion-association complex as liquid membrane for the determination of tantalum by ion-selective electrode.

the optimal conditions, and

5. to study the analytical applications of the newly made membrane electrode for determination of tantalum in real, Ethiopian tantalite-columbite ore, and artificial samples by different potentiometric measurement techniques.

2. THEORETICAL CONSIDERATIONS

2.1 Ion-Selective Membrane Electrodes

Ion-selective electrodes(ISEs) have been the subject of rapidly increasing interest over the past twenty years and their development has opened up a large new fields of potentiometry. The speed at which these fields have developed is a measure of the degree to which the electrodes meet the necessary requirements for rapid, accurate and low cost analysis39.

The term "ion-selective electrode" is applied to a range of membrane electrodes which respond selectively to one (or several) ionic species in the presence of others40. They are, in practice, based on elecrochemical membranes, i.e., on phases consisting solid or liquid electrolytes, perfectly separating two electrolyte solutions41.

The word membrane is used, in its broadest sense, to denote a thin section of conducting material that regulates the movement of charged species across it, thereby creating conditions for the generation of an electric potential42. It is used, in a phenomenological sense, to indicate all types of electrodes that act reversibly as a membrane electrode, irrespective of the mechanism involved. Most of the membranes used as electrodes require selectivity, without being ion specific,i.e., not equally permeable to all components. Such membranes are called semi-permeablae membranes. In chemistry, membranes separating two electrolytes, which are not equally permeable to all kinds of ions and also semi-permeable, are termed as electrochemical

membranes40-42. An important property of electrochemical membranes is the electric potential difference that arises between the separated solutions. This difference is called the membrane potential.

Ion-selective electrodes are characterized by phase boundaries at which the electrical potential difference are caused by distribution of ions between the two phases, i.e., by boundaries between two electrolytes, either solid-liquid or liquid-liquid. At the membrane of ion-selective electrodes, there are two basic phenomena occuring at interface between the two electrolytes, without which one cannot explain the membrane potentials of permselective membranes41. First, the diffusion potential, which is strongly reflected in, for example, the liquid junction potential and results from differnt mobilities and concentration of the ions in the electrolytes in contact. Secondly, there is the Donnan potential, which results from complete hindrance to the transfer of one or more kinds of ions across the interface between two electrolytes.

Elecrical potential arising across the membrane when they seperate two electrolyte solutions may be called membrane potential. The potential may arise as a diffusion potential across the membrane due to differences in the mobilities of the ions. There are also other ways in which a potential might arise across the membrane. The simplest way is to have it arise as an ohmic potential drop by passing electric current from an external source of emf through the system. Another way would be to have it arise as a static potential by adding to one of the components

some charged species that cannot pass through the membrane.

Ion-selectilve elctrodes are used for the determination of potential(membrane potential) which is depndent on the concentration (more precisely the activity) of a particular ion in solution. The potential arise across the electrode/electrolyte interface43.

The potential measurement with ion-selective electrode is performed by using the electrochemical cell of the following type(Fig. 1).

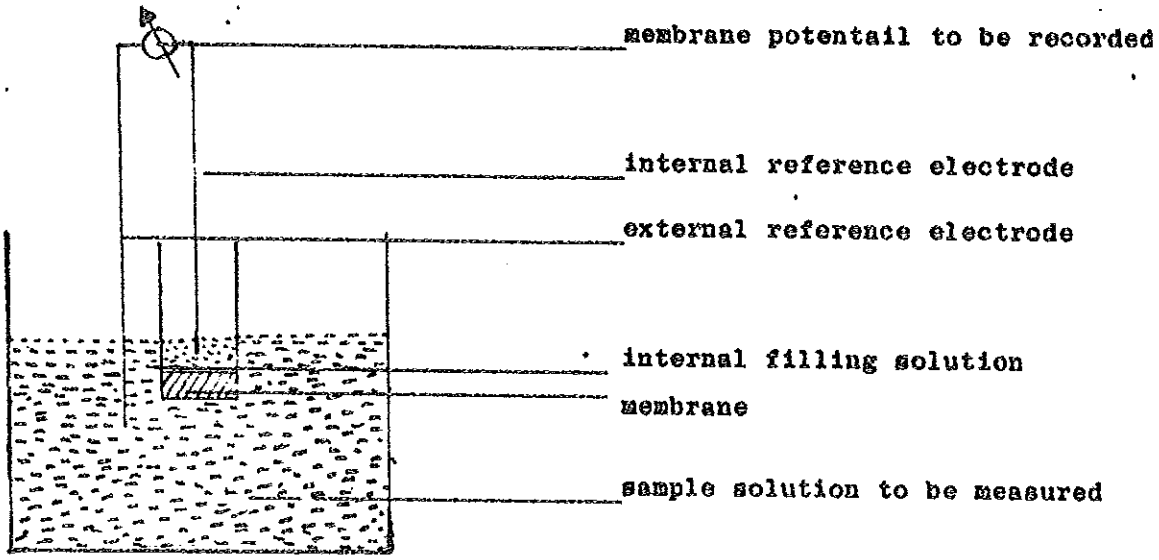

Fig. 1. Schematic representation of membrane electrode cell assembly

The potentials cannot be determined directly, but can easily be derived from the emf values for the complete cell using the Nernst equation. These cells comprise the membrane, which is usually in contact, on one side with a solution conatining the ions of interest (solution 1) and a suitable reference electrode

and, on the other side, with the test solution, in which the external reference electrode is immersed (solution 2). A schematic representaion of this cell assembly is shown in cell I:

Solution 1 | Membrane | Solution 2 cell-I

2.2 Potentiometric Seictivity Coefficient

The selectivity of an electrode is determined by its ability to distinguish between different ion species present in the contact solution. An electrode is ideally selective, i.e., specific, when its potential is not affected by ionic species present in the sample solultion other than the ion for which the electrode is selective44. However, not only the ion mobility and strength of association between the ions determine the selectivity, but also factors such as the ionic strength and the ion concentraion ratio contribute a lot. Thus, if another ion, called interfering ion, j, is present together with the ion of interest, called primary ion, i, in the sample solution the electrode potential will have contributions from both the primary and interfering ions45-47.

For ion-exchange reaction of the type:

$$\bar{i} + j \rightleftharpoons \bar{j} + i \qquad (2.1)$$

the diffusion potential is given by:

$$\varphi = \frac{nRT}{F} \ln \frac{(ai')1/n + (\bar{u}j/\bar{u}i)\, K1/n\, (aj')1/n}{(ai')1/n + K1/n\, (aj')1/n}$$

$$-\frac{nRT}{F} \ln \frac{(ai'')1/n + (\bar{u}j/\bar{u}i)\, K1/n\, (aj'')1/n}{(ai'')1/n + K1/n\, (aj'')1/n} \qquad (2.2)$$

where n depends only on the membrane properties. That is for the special case of the so-called n-type membrane, the following relation holds between the ion activity in the membrane and its concentration.

$$\frac{d \ln \bar{a}j}{d \ln Cj} = \frac{d \ln \bar{a}k}{d \ln Ck} = n \qquad (2.3)$$

For ion-exchange reaction, (2.1), the two phase boundary or Donnan potentials were derived by Dole48 and Nicolsky49 for n = i, and expreesed as

$$E' = \text{constant} + \frac{nRT}{F} \ln (ai1/n + K1/n\, aj1/n) \qquad (2.4)$$

The total potential,E, is the sum of two phase boundary potentia-l, E′ and E", and a diffusion potential(ψ)

$$E = E' - E'' + \psi \qquad (2.5)$$

Thus, the total potntial is obtained by adding equations (2.2) and (2.4) which gives:

$$E = \frac{nRT}{F} \ln \left[\frac{(ai')1/n + (Kpot\ aj')1/n}{ai'')1/n + (Kpot\ aj'')1/n} \right]$$

where Kpot = K ($\bar{u}j$ / $\bar{u}i$)n has been called the electivity coefficient which includes both the chemical a d the mobility factors; and K is the equilibrium constant for the ion-exchange of equation (2.1) and given as:

$$K = \frac{\bar{a}j\, ai}{aj\, \bar{a}i} \qquad (2.7)$$

If the concentrations on one side(") are held constant, as in a practical membrane electrode unit, equation (2.6) reduces to:

$$E = \text{constant} + \frac{nRT}{F} \ln [ai1/n + (Kpot_{ij}\ aj)1/n] \qquad (2.8)$$

Equation (2.8) is valid for a monovalent ion in the presence of another monovalent ion. Garrels50 and co-workers have given equations applicable to divalent ions in the presence of monovalent ions, namely,

$$E = \text{constant} + \frac{nRT}{2F} \ln ((ai2+)1/n + [Kpot_{ij}\ (aj+)2]1/n) \qquad (2.9)$$

and divalent ions in the presence of other divalent ions, namely,

$$E = \text{constant} + \frac{nRT}{2F} \ln ((ai2+)1/n + (Kpot_{ij}\ aj2+)1/n) \qquad (2.10)$$

These equations for n = 1 may be written in the general form of the extended Nicolsky equation51.

$$E = \text{contant} \quad \frac{RT}{ziF} \ln [ai + \sum_{i \neq j} Kpot\ (aj)^{z_i/z_j}] \qquad (2.11)$$

where i is the primary ion of the valence zi to which the membrane electrode is selective and j is the interfering ion of valence zj; the plus sign is for cations and minus for anions.

Thus, the potentiometric selectivity coefficient, Kpot, expresses the degree of selectivity of the electrode to the primary ion, i, with respect to the interfering ion, j.

It represents the sensitivity ration: interfering ion/measured ion44. Thus, if Kpot) i, the selectivity of the

electrode to the interfering ion, j, is more than to that of the primary ion, i. On the other hand, if $K_{ij}^{pot} < 1$, the electrode is more selective to the primary ion, i, than the interfering ion, j.

Determination of the Selectivity Coefficient. In the ideal case, ion-selective electrodes should meet the basic assumption that they exhibit Nernstian response towards the activity of the ion to which they are selective. Furthermore, the measured selectivity coefficient values should not magnify the effect of the interfering ion. In practice, this does not happen since some theoretical assumptions are not being fulfilled. The relevant assumptions are, for example41:

(i) sufficiently rapid establishment of ion-exchange equilibrium, the rate of which may actually depends on the concentrations of both the ion to be determined and the interfering ion;

(ii) maintenance of the same conditions in the solution at the membrane surface as those in the bulk of the solution;

(iii) the theory generally assumes a simple membrane mechanism.

A number of methods have been described for the experimental determination of the selectivity coefficient46,52,53. These methods fall into two categories,

(i) the separate solution method and (ii) the mixed solution method.

(i) Separate Solution Method. The potential of the elctrode is

measured first in solutions containing the primary ion, with no interfering ion, and then in solution containing the interfering ion without primary ion.

Method 1. The potential of an ion-selective electrode in a solution containing only the primary ion, i, (i.e., aj = 0) is given by:

$$Ei = Eo \pm \frac{RT}{ziF} \ln ai \qquad (2.12)$$

If the solution is without i (i.e., ai = 0) and contains only ion j, equation (2.11) becomes:

$$Ej = Eo \pm \frac{RT}{ziF} \ln K^{pot}_{ij} (aj)^{z_i/z_j} \qquad (2.13)$$

For the condition ai = aj, equation (2.12) and (2.13) give the relation:

$$\pm \frac{(Ej-Ei)}{S} = \log K^{pot}_{ij} + \left(\frac{zi}{zj} - 1\right) \log ai \qquad (2.14)$$

where S = 2.303 RT/ziF or the experimental slope, Ej and Ei are in millivolts.

Method 2. If the concentrations of the solution of ion, i, and of the solution of ion j are chosen such that Ei = Ej, then equation (2.12) and (2.13) give 44:

$$ai = K^{pot}_{ij} (aj)^{z_i/z_j} \qquad (2.15)$$

(ii) Mixed Solution Method. Both ions i and j are in same solution in this method. This involves the measurements of the potentials of solutions containing a fixed quantity of the interfering ion, j, and varied quantity of the primary ion40. Ideally the values of the selectivity coefficient can be calculated from equation (2.15), ai and aj being the

activities that are determined from the plot of the measured potential versus pai (Figs. 2 and 3).

Method 1. This method depends on finding graphically the point T at which the electrode is responding equally to both ions. If the line RS is straight and parallel to the abscisse, then T is the point of intersection of the extrapolation of PQ and SR K^{pot}_{ij} may then be calculated from the activity of i at point T, Tai, and the constant aj by means of the equation39,54.

$$K^{pot} = \frac{Tai z_j}{aj z_i} \qquad (2.16)$$

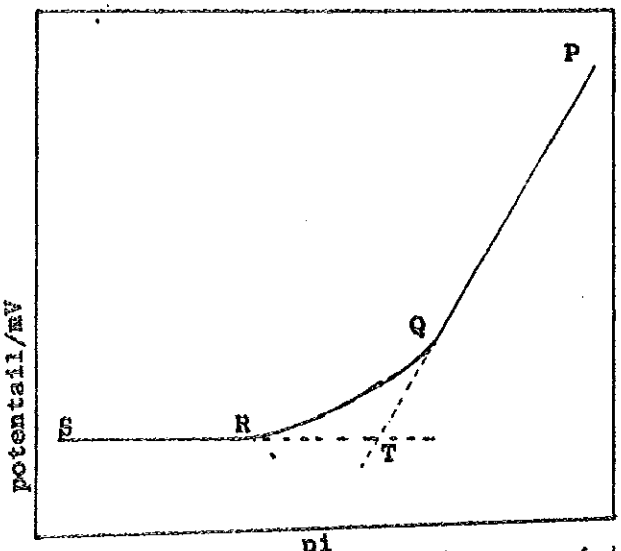

Fig.2. Typical curve for calculations of K^{pot}_{ij} by mixed solution method (method 1).

The method is only suitable if RS is a straight line.

Method 2. The more generally applicable method is one that does not depend on the form of RS, but instead relies on PQ and QR (Fig.2). From equation (2.11) both ions are contributing equally to the electrode response when39

$$ai = K^{pot}_{ij}\, aj z_i / z_j \qquad (2.17)$$

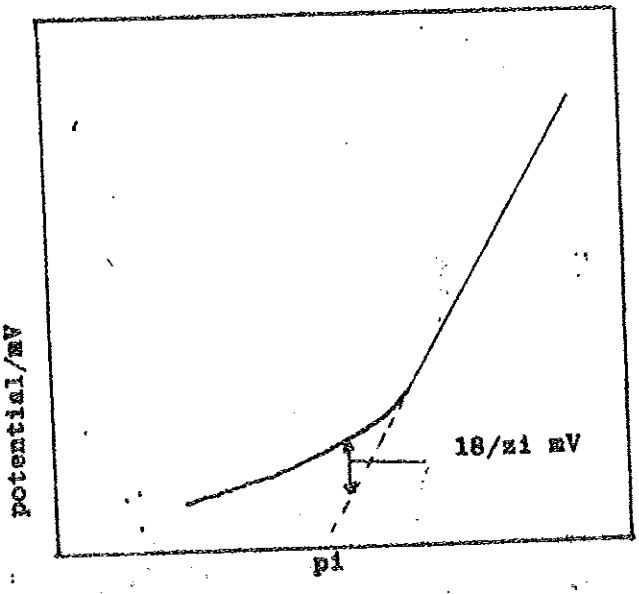

Fig.3. Calibration graph, illustrating Method 2 for determination of selectivity coefficient by mixed solution method.

If the activity of i at which this equality occurs is ai', and the activity of j is aj, then the potential is given by:

$$E = Eo + \frac{2.303\ RT}{ziF} \log10\ (2ai') \qquad (2.18)$$

The response of the electrode in the absence of j is given by the extrapolation of PQ as far as the limit of Nernstian response. The difference between the electrode potentials in solutions of i with activity ai' with and without j at activity aj' is therefore given by 39:

$$E = \frac{2.303\ RT}{ziF} (\log10\ 2ai' - \log10\ ai')$$

$$= \frac{2.303\ RT}{ziF} \log10\ 2$$

$$= 18/\ zi\ mV \text{ at } 25oC$$

Thus by finding on the graph, the activity of i at which the experimental line QR differs from the extrapolation of PQ by 18/zi mV (as in Fig. 3) the activity ai is determined.

important and widely used techniques are briefly discussed below.

Calibration Method. Empirical calibration curves, where by the electrode potential is related to the logarithm of activity or concentration of the ion of interest, is most straight forward technique and is the technique of choice whenever possible. The sample to be analysed is pretreated as required and the electrodes are immersed in it. The equilibrium cell potential is then measured and related to the determinand activity or concentyration by means of the calibration graph89.

A series of solution can also be prepared spanning the anticipated range of activity or concentration of the determinand in the sample. If the calibration graph is expected to be linear with close to the theoretical Nernstian slope in the measurement range, and the range is broad, it is usually sufficient to prepare one standard per decade of activity or concentration. The determination of the sample concentration can then be made by single-point calibration. It follows from the Nernst equation that:

$$E_{sample} - E_{standard} = S \log \frac{a_{sample}}{a_{standard}} \qquad (2.20)$$

which can be rearranged to give

$$a_{sample} = a_{standard}\ 10^{\Delta E/S} \qquad (2.21)$$

where S is the experimental slope whose value can be determined using two standard solutions of known differnt concentrations. This approach requires no knowledge of the standard potential of the electrode pair. The assumption here is that the value of the

slope is constant and there is a linear relationship between the potential and log activity.

A more complex version of this method can also be considered. This involves the use of two standard solutions in which the determinand concentrations are as_1 and as_2, which bracket the unknown concentration Cx. Then applying the Nernst equation to all these three solution, Cx can be calculated from:

$$\frac{(Ex - Es_1)}{(Es_1 - Es_2)} \log \frac{as_1}{as_2} = \log \frac{ax}{as_1} \qquad (2.22)$$

The method does not require the knowledge of standard potential or slope. Moreover, the method will compensate for slow drift in both parameters, and a linear response over the range of intersest can be assumed.

Standard Addition Technique. This method is useful for the types of analysis; the rapid and approximate analysis of occasional samples and, more importantly, the determination of the total concentration of determinand in samples in which the determinand is partially complexed39.

In standard addition method (alternatively called the 'known addition method') a known volume, Vs, of the standard solution of concentration Cs is added to the sample solution, Vx ml, containing unkown concentration, Cx, and the potential change of the electrode is recorded42.

The observed initial potential of the sample solution of unkown concentration, Cx, is given by the Nernst equation. Thus,

$$E1 = Eo \quad \frac{RT}{ziF} \ln (Cx\, Y x) + EL \qquad (2.23)$$

EL being the liquid junction potential.

On addition of a known amount of test ion, (Vs ml of known concentration, Cs, to the initial volume, Vx), the new potential measured is given by:

$$E2 = Eo \quad \frac{RT}{ziF} \ln \frac{CxVx + CsVs}{Vx + Vs} \gamma x' + EL \qquad (2.24)$$

Assuming the constance of EL and $\gamma x = \gamma x'$, subtracting equation (2.23) from equation (2.24) gives:

$$E = E2 - E1 = \frac{RT}{ziF} \ln \frac{CxVx + CsVs}{(Vx + Vs)\,Cx} \qquad (2.25)$$

On rearrangement of equation (2.25), it gives:

$$\frac{\Delta E}{S} = \log \frac{CxVx + CsVs}{(Vx + Vs)\,Cx} \qquad (2.26)$$

where S is the Nernst slope (= 2.303 RT/ziF), experimentally determined by using a series of know standard solutions. Equation (2.26) may be rearranged to give:

$$Cx = \frac{CsVs}{Vx+Vs\ \gamma} 10^{\Delta E/S} - \frac{Vx}{V_x + V_s} 1-1 \qquad (2.27)$$

Thus, Cx can be determined.

If the change in volume of the sample, upon addition of the standard is negligible (i.e., Vx)) Vs) then equation (2.27) becomes:

$$Cx = Cs\ (Vs/Vx)\ (10^{\Delta E/S} - 1) \qquad (2.28)$$

or

$$\Delta E = S \log \left(1 + \frac{CsVs}{CxVx}\right) \qquad (2.29)$$

or

$$(10^{\Delta E/S} - 1) = \frac{Cs}{CxVx} Vs \qquad (2.30)$$

Equation (2.30) indicates that Cx may be calculated from the single addition method or preferably determined from the slope of aplot of $10^{\Delta E/S} - 1$ vs Vs where several addition of standard are made.

Advantages of this technique over other techniques are that electrode calibrationis unnecessary,only one standard solution is required and calibration drift is unimportant; however, two potential measurements per sample are necessary59,60.

Sample Addition Technigue. This method is the reverse of the foregoing one, and also called the "analyte addition" technique. First potential of a know volume, Vs, of the standard solution of a know concentration, Cs, is measured. Then, a known volume, Vx, of the solution to be analysed is added, and the new potential is measured. The concentration of the unknown sample solution, Cx, can be calculated from the equation41-44.

$$Cx = Cs \left[\frac{(Vx+Vs)}{Vx} 10^{\Delta E/S} - \frac{Vs}{Vx} \right] \qquad (2.31)$$

This rearranged equation is derived by replacing Cs in place of Cx in equation (2.24) and subtracting from equation (2.25).

Gran's Plots. The methods were devised by Gran61 in 1952 as a way of linearizing the data obtained from multiple standard addition procedure in potentiometric titrations and thus easily and precisely locating the equivalnence point of titrations62,63.

The theory associated with these plots is straight forward. Equation (2.24) can be rearranged to give:

$$(Vx + Vs)\ 10^{E2F/2.303\ RT} = 10^{(E + E')/2.303\ RT}\ Yx' \times (CxVx + CsVs) \qquad (2.32)$$

A plot of $(Vx + Vs)\ 10^{E2F/2.303\ RT}$ vs Vs gives a straight line which intercepts the abscissa for value of Vs called Ve; where CxVx = -CsVe.

Thus, Cx can be calculated since Ve, Vx and Cs are known. The technique may also be applied to both complexometric and precipitation titrations.

Standard Subtraction Method. The standard or known subtraction method is differnt only in that the standard solution added to the sample is not a determinand solution but a solution of a species which reacts quantitatively with the determinand. Thus a decrease in determinand concentration is produced with corresponding cahnge in cell potential. This potential change may be used to calculate the initial determinand concentration in the sample by means of the following equation derived in a similar manner to equation (2.27).

$$Cx = \frac{CsVs}{Vx - (Vs + Vx)\ 10^{\Delta E/S}} \qquad (2.33)$$

The assumption here is that, a 1:1 stoichiometry of the reaction between the determinand and the added species is considered. The equation becomes more complex if there is a differnt stoichiometry[39,64].

3. EXPERIMENTAL

3.1. Materials and Reagents

Brilliant green (Fluka), 40 % (w/w) hydrofluoric acid (Analar, Hopkin and Williams, and BDH), 98 % (W/W) sulphuric acid (BDH), tetrahydrofuran (Riedel-de Haen), PVC (Fluka), nitrobenzene (Riedel-de Haen), 1-chloronaphthalene (Fluka), chloroform (Riedel-de Haen), chlorobenzene (BDH), 1,2-dichloroethane (Fluka), 1,2-dichlorobenzene (BDH), anhydrous sodium sulphate (Riedel-de Haen), ammonium fluoride (Riedel-de Haen), tetraphenylarsonium chloride (Fluka), potassium nitrate (BDH) and potassium carbonate (BDH) were used without further purification.

3.2 Preparation of Solutions

3.2.1 Preparation of Tantalum Solution. Accurately weighed, 1 g of a well-powdered Ta_2O_5 (BDH, 99.9 %) was intimately mixed with 2.5 g of K_2CO_3 and 2.5 g of KNO_3 (2:5:5 weight ratio) in a platinum crucible. The mixture was fused in a muffle furnace at 740-760oC for about 15 min. The fused melt was cooled to room temperature and treated with about 25 ml of concentrated sulphuric acid. The extract was quantitatively transferred to a 300 ml Kjeldhal flask, evaporated to dryness, and cooled. The residue was dissolved in 100 ml of 20 % (w/v) tartaric acid by heating and continuously swirling. A clear solution was obtained, and it was quantitatively transferred to a 250 ml volumetric flask and made up to the mark with 20 % (w/v) tartaric acid[65,66].

3.2.2 Standardization of Tantalum Solution. A 9 ml aliquot of tantalum stock solution was transferred into a 600 ml beaker. To this was added 10 ml of concentrated nitric acid and the solution was diluted to 200 ml with distilled water. About 1 g of NH4F was added to the solution and the content was gently heated over the steam bath for 15 min67. A 5 ml aliquot of 2 % (w/v) tetraphenyl-arsonium chloride was added dropwise and allowed to stand for 30 min to ensure the complete precipitation of tantalum(V) as TaF_6^- Ph_4As^+. The precipitate was filtered and then ignited in a porcelain crucible for one hour. The residue was cooled to room temperature and weighed as Ta_2O_5. The weight of Ta_2O_5 was found to be 35.8 mg. The concentration of tantalum(V) stock solution was found to be 1.80 X 10-2 M.

3.2.3 Preparation of Sample Solutions. Accurately weighed, 0.5 g of a well-powdered Ethiopian tantalite-columbite ore samples were intimately mixed with 1.25 g of K_2CO_3 and 1.25 g of KNO_3 (2:5:5 weight ratio) in a platinum crucible. The mixture was fused in a muffle furnace at 740-760oC for about 15 min. The fused melt was cooled to room temperature and treated with about 25 ml of concentrated sulphuric acid. The extract was quantitati-vely transferred to a 300 ml Kjeldhal flask,evaporated to dryness,and cooled. The residue was dissolved in 80 ml of 25 % (w/v) tartaric acid by heating and continuously swirling. The solution obtained was then quantitatively transferred to a 100 ml volumetric flask and made to volume with 20 ml of 5 M sulphuric

niobium pentoxide (Johnson and Mathey 99 %) with 3.6 g of potassium pyrosulphate (Riedel-de Haein) in silica crucible[68,69]. The cooled melt was dissolved in 100 ml of 20 % (w/v) tartaric acid (BDH, Analar) solution by heating over sand bath. The solution was cooled, then transferred to a litre volumetric flask, and diluted to volume with distilled water.

The solution of Ti(IV) was prepared by fusing 0.4 g of TiO2 (BDH) with 4 g potassium hydrogen sulphate (BDH). The cooled melt was leached with 10 % (v/v) sulphuric acid and diluted to 100 ml with 10 % (v/v) sulphuric acid[69].

Solutions of Er(III), Zr(IV) and Bi(III) were prepared by dissolving europium oxide, zirconium chloride and bismuth nitrate (BDH), respectively, in 1.0 M hydrochloric acid solution. The dissolution was carried out by heating to obtain a clear solution.

Solutions of Al(III) , Hg(II) and Ce(IV) were prepared by dissolving the respective sulphate salts (BDH or Riedel-de Hean) in 0.5 M hot suplhuric acid solution.

Solutions of Fe(III), Zn(II), Cu(II), Ni(II), Ca(II), Cd(II), La(III), UO2(II), Pb(II), Y(III) and Ag(I) were prepared by disolving the respective nitrate salts (BDH or Riedel- de Hean) in distilled water. Solutions of Mn(II) and Co(II) were prepared by dissolving the respective sulphate salts (BDH or

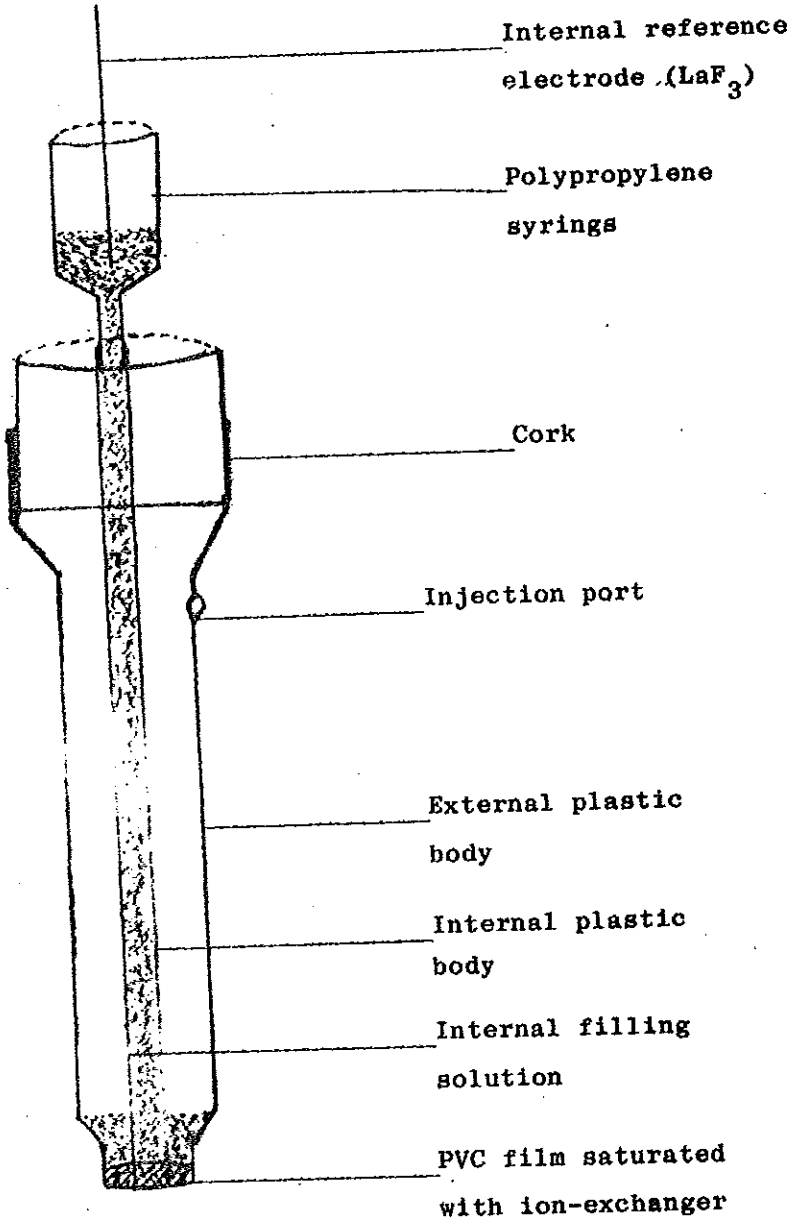

Fig. 4. Liquid membrane electrode.

polymer powder in 4 ml of tetrahydrofuran containing 10 drops of 1-chloronaphthalene[32,37,70].

The narrow tip of the plastic body was carefully dipped into the PVC solution three times with the interval of 2 min until the thickness of the matrix formed was 2-3 mm. Care has been taken to avoid the impregnation of air bubbles into the PVC matrix. The electrode body, along with the PVC support, was suspended with the PVC held downwardsd in the hood for 24 h, to get the solvent evaporated. A white film of PVC matrix was obtained.

3.3.2 Preparation of Electroactive Material. Aliquots of 30 ml of 1.80 X 10-2 M tantalum(V) stock solution, 2.7 ml of concentrated sulphuric acid, and 2.3 ml of 40 % (w/w) hydrofluoric acid were transferred into 250 ml polypropylene separtory funnel. To this was added 6.25 ml of 2.0 X 10-2 M Brilliant Green solution, and the volume of the aqueous phase was adjusted to 50 ml with distilled water. The mixture was shaken vigoruously, for five min, with 25 ml of nitrobenzene (five times in 5 ml portion), and the two phases were allowed to separate for 15 min during each extraction. The organic phase was collected into a 50 ml plastic beaker containg about 2 g anhydrous sodium sulphate. The dried extract was transferred into a 25 ml volumetric flask. The sodium sulphate crystals were washed with few drops of fresh nitrobenzene, the washing were added to the volumetric flask, and the coloured extract was diluted to volume with nitrobenzene.

This solution, i.e., the solution of Brilliant Green-hexafluorotantalate(V) ion-association complex in nitrobenezene, was used as a liquid membrane.

Lower concentrations of the electroactive material were prepared by diluting the extract with fresh nitrobenzene.

3.3.3 Preparation of Briliant Green-Hexafluorotantalate(V) Liquid Membrane Eelectrode. Aobut 2-3 ml of the Brilliant Green-hexafluorotantalate(V) extract in nitrobenzene was introduced into the outer jacket of the ectrode body through the injection port. The inner tube of the electrode body was filled with the solution that was 1.0 X 10-2 M in Ta(V), 1.0 M in H2SO4 and 1.0 M in HF, up to a point such that the lower end of the fluoride-selective electrode, which was used as an internal reference electrode, was in contact with the inner filling solution. The narrow tip of the electrode was immersed into the solution of the same compostion as that of the inner filling solution and was kept in this solution for 36 h for conditioning. At this point the electrode was ready for use. When not in use the electrode was kept in the condtioning solution.

3.4 Instrumentation

The potential measurement of the the test solutions were made using Philips P W 9404 digital pH mV meter equipped with external ground glass diaphragm reference electrode against the

Brilliant Green-hexafluorotantalate(V) liquid membrane electrode. Equilibrium potentials of the test solutions were recorded after continuous stirring with a Teflon coated stirring bar for 1-2 min to obtain a constant potential reading at room temperature (20 ± 2oC). The complete cell is schematically represented as follows.

LaF3	Internal solution	Liquid membrane	Test solution	Ag/AgCl plastic body electrode	cell-II

Internal reference electrode — Liquid membrane electrode — external reference electrode

3.5 General Procedure

3.5.1 Study of the electrode Behavior. Aliquots (2-12 ml) of 1.80 X 10-2 M tantalum(V) stock solution were transferred into 100 ml polypropylene beakars. Concentrated sulphuric acid (1.1 ml) and 40 % (w/w) hydrofluoric acid (0.9 ml) were added to the solutions and the solutions were diluted to 20 ml with doubly distilled water. Serial dilutions were made in the same manner to get test solutions, which were 1.0 X 10-7- 1.0 X 10-2 M with respect to tantalum(V) and 1.0 M with respect to both sulphuric acid and hydrofluoric acid.

The liquid membrane elecrode and the external reference electrode were dipped into 20 ml of the stirred solutionsin 100 ml polypropylene beakers. Aconstant potential was recorded within 20-120 seconds. All potential measurements were made at room temperature (20 ± 2oC).

coefficients were evaluated from the calibration curve, in the presence of each interfering ion, using equation (2.19).

3.7. Procedures for Sample Analysis

3.7.1 Direct Potentiometry39. The potentials of aliquots (20 ml each) of the sample solutions in 1.0 M sulphuric acid and 1.0 M hydrofluoric acid were measured following the general procedures described for electrode behavior. The tantalum concentration in the sample solutions was determined from the calibration curve (E, mV, vs log Ta^{5+}). Alternatively, the concentration of tantalum in the sample solution can be calculated based on the single-point calibration64 using equation (2.20) or by use of two standard solutions in which the analyte activities are as and as40 from equation (2.22).

3.7.2. Standard Addition Technique. The potentials (Ex) of 20 ml (Vx) of a hundred times diluted sample solution of concentration Cx, in 1.0 M sulphuric acid and 1.0 M hydrofluoric acid was first measured. This was followed by addition of 1 or 2 ml of 2.0×10^{-3} M standard tantalum(V) solution in 1.0 M sulphuric acid and 1.0 M hydrofluoric acid to the stirred sample solution and the new potential, Es, was recorded. The concentration of the sample solution was claculated by equation (2.27)39.

3.7.3 Sample Addition Technique72,73. The potential (Es) of 20 ml (Vs) of 2.0×10^{-5} Mtantalum solution in 1.0 M sulphuric acid

4. RESULTS AND DISCUSSION

4.1 Arrangement of the Cell Assembly

Glass and plastic tubes, both with PVC support, were tried as the electrode body for the liquid membrane electrode. These electrodes were examined with different combinations of different internal and external reference electrodes to give the complete cell assembly for potential measurements.

Hg/Hg2Cl2/Cl- (glass body)	Test solution	BG+TaF6- liquid membrane (in glass)	Inner filling solution (in glass)

cell-III

Ag/AgCl (glass body) Hg/Hg2Cl/Cl- (glass body)	Test solution	BG+TaF6- liquid membrane (in plastic)	Innner filling solution (in plastic)

cell-IV

Ag/AgCl (Glass body) Ag/AgCl KCl,sat.	PVC-KCL sat.	Salt bridge	Test solution	Liquid memb.	Inner filling solution

cell-V

salt bridge	PVC-KCL sat.	Ag/AgCl KCl,sat.			
Ag/AgCl KCl,sat.	Agar-KCl sat.	salt bridge	Test solution	Liquid memb.	Inner filling solution

cell-VI

salt bridge	Agar-KCl sat.	Ag/AgCl KCl,sat.		
Ag/AgCl (plastic body) LaF3 (F- selective)	Test solution	BG+TaF6- liquid memb. (in plastic)	Inner filling solution (in plastic)	

cell-VII

The cell assemblies consisting of the liquid membrane electrode made of either glass of plastic tubes connected with the internal and external reference electrodes both made of glass bodies (cell-III and cell-IV) were found not useful because of the drift in cell potential. This may probably be due to the reaction of hydrofluoric acid with glass which resulted in the formation of fluoroborate complexes. Thus, the total avoiding of glass contact with hydrofluoric acid was necessitated. For this reason the liquid membrane electrode made of plastic tubes was connected with internal and external reeference electrodes both made of glass bodies via either PVC-KCl40 or agar-KCl43 salt bridges to give the cell assemblies which were free from the direct contact of hydrofluoric acid with glass (cell-V and cell VI). However, these cell assemblies were also found to be not useful. In these cell assemblies, the connection of the salt bridges with the liquid membrane and reference electrodes were made by flexible plastic tubes of different dimensions. The problems arised with these tubes were breakage of the junction and leakage of the solution which introduced empty spaces in the tubes.

The cell assembly consisting of the liquid membrane electrode made of plastic tubes connected with Ag/AgCl (ground glass diaphragm, fluoride resistant) external reference electrode and LaF3 (fluoride selective) internal refereence electrode (cell-VII) was found to be the most suitable for the study of the behavior of the liquid membrane electrode. Hence, all subsequent studies were made with this cell assembly.

4.2 Selection of Membrane Solvents

The choice of solvents has a drastic effect on the selectivity of the membrane. The selectivity of the membrance electrode is governed by both the mobility of the ions in the membrane and the equilibrium that exists at the membrane solution interfaces (partition coefficents, ion-exchange equilibrium constants, ion-association constants). These parameters are influenced by the properties of the organic solvants used in liquid membrane prepatation42,75,76.

Thus, the solvent used in liquid membrane electrode must (a) be quite insoluble in water, (b) have a low vapour pressure, (c) have a sufficiently high viscosity not to pass through the membrane skeleton quicly and, (d) allow considerable association of ions in the membrane41.

Based on these requirements and other properties, Table 1. five solvents; namely, nitrobenzene, chlorobenzene, 1,2-dichlorobenzene, 1,2-dichloroethane and chloroform were tested as membrane solvents in the present investigation.

Table 1. Properties of selected organic solvents77

Solvent	B.P.oC (1 atm.)	ϵ (25oC)	η(30oC) poise	solubility (25oC) (% w/w)	Density g/ml (25oC)
Nitrobenzene	210.80	34.82	1.634	0.19	1.19835
Chlorobenzene	131.68	5.62	0.715	0.048	1.10630 (20oC)
1,2-Dichloro-benzene	180.48	9.93	1.325 (25oC)	<0.026	1.30
1,2-Dichloro-ethane	84.48	10.36	0.780	0.81	1.2458
Chloroform	61.15	4.81 (20oC	0.514	0.072	1.480

The ion-association complex of Brilliant Green-hexafluorotantalate(V) was extracted into each of these solvents from the awueous phase which was 1.0 M with respect to boty sulphuic and hydrofluoric acid. However, the extraction of Brilliant Green-hexafluourotantalate(V) (BG+TaF6-) ion-association complex was found to be I:ncoplete in all the solvents (probably due to lower dielectric constants) except in nitrobenzene in which the extraction of the complex was complete at the required connectration level (1.0 X 10-2 M BG+TaF6-). Because of the partial extraction of the ion-association complex in most of the solvents, the completeness of the extraction was assessed only qualitatively. The extraction was considered to be complete when the aqueous phase left after extraction was colourless.

Thus, no potential measurement was performed in the solvents other than nitrobenzene, since it was not possible to estimate the concentration of electroactive material in the membrance. Nitrobenzene, having low miscibility with the aqueous phase, higher boiling point, high viscosity and higher dielectric constant (Table 1) which fulfills most of the requirements of the membrane solvents was the solvent of choice.

4.3 Influence of Exchanger Concentration

Five different concentrations of the exchanger, Brilliant Green-hexafluorotantalate(V) (BG+TaF6-) were examined to study the behavior of the liquid membrane; namely, 5.0 X 10-4 M, 1.0 x 10-3 M, 2.0 x 10-3 M, 5.0 X 10-3 M and 1.0 X 10-2 M BG+TaF6- in nitrobenzene. The electrode with exchanger concentrations, i.e., 5.0 x10-4 and 1.0 X 10-3 M gave unstable potential readings even after five minutes. this probably be due to the the higher resistance of the organic matrix. Therefore, except for initial trials,no potential measurements have been made with these electrodes.

The elecrode with 2.0 x10-3 M BG+TaF6- gave a linear response in the range of 5.0 X 10-6- 1.0 X 10-2 M tantalum(V) with the average slope of -58 ± 2 mV per decade,but the time requiredto a constant potential readings was more than two minutes. The electrode with 5.0 X 10-3 M exchanger concentration gave a linear response in yhe range of 2.0 x 10-6 - 1.0 X 10-2 M

tantalum(V) with the average slope of -58.5 ± 1.5 mV per decade. The electrode with 1.0 X 10-2 M BG+TaF6- showed linearity between 1.0 X 10-5 - 1.0 X 10-2 M tantalum(V) with the average slope of -58 ± 2 mV per decade. With the latter two electrodes,- the constant potential readings were obtained within two minutes. A somewhat narrow linear range with the electrode of highest concentration, 1.0 X 10-2 M BG+TaF6-, can probably be accounted to the elution of membrane solute into the adjacent aqueous solutions. Therefore, the elecrode with 5.0 X 10-3 M BG+TaF6- was chosen for further study because of the wider response range and better slope. These results are summarized in Table 2 and the curves are shown in Fig 5.

At least 36 h of saturation time was found to be necessary in order to obtain a constant potential readings with the liquid membrane electrode of 5.0 X 10-3 M BG+TaF6-. Longer saturation time has been found to have no adverse effect on the electrode response behavior.

Table 2. Reponse range and slope of BG+TaF6- liquid membrane electrode

[H2SO4] = 1.0 M ; [HF] = 1.0 M

Exchanger concentration in the electrode, BG+TaF6- M	Linear range Ta(V), M	Slope* mV per decade
2.0 x 10-3	5.0x10-6-1.0x10-2	-58 2
5.0 x 10-3	2.0x10-6-1.0x10-2	-58.5 1.5
1.0 x 10-2	1.0x10-5-1.0x10-2	-58 2

* Average of triplicate measurements.

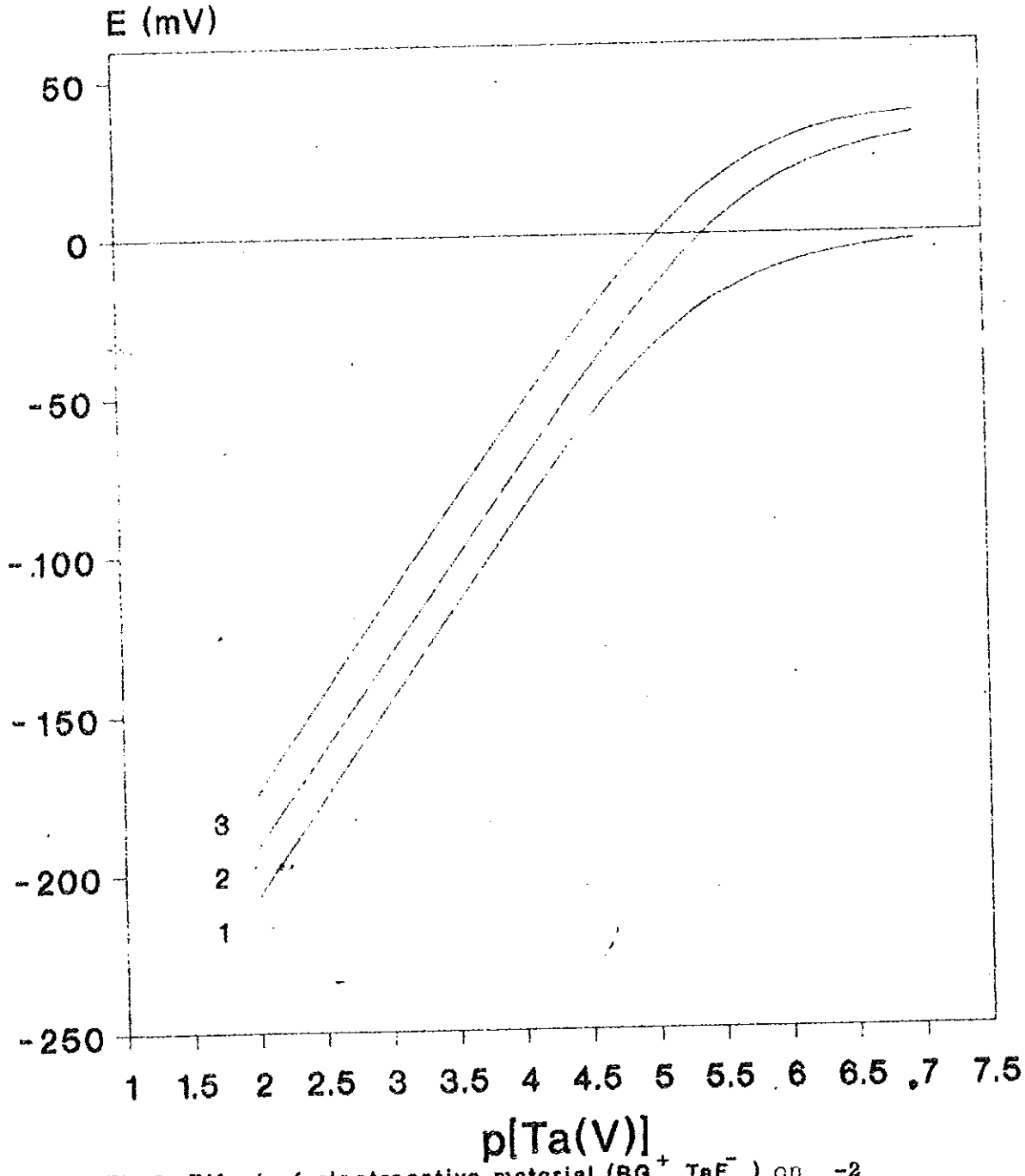

Fig.5. Effect of electroactive material ($BG^{+}\ TaF_6^{-}$) on the response behaviour of the electrode, (1) 1.0×10^{-2} M (2) 5.0×10^{-3} M (3) 2.0×10^{-3} M

Table 3. Effect of the concentration of sulphuric acid on the slope of the BG+TaF6- liquid membrane electrode*

[HF] = 1.0 M

H2SO4, M	Slopea mV/decade	Slopeb mV/decade	Slopec mV/decade
0.0**	-59.9	-57.5	-34.9
0.5	-58.9	-58.2	-38.2
1.0	-58.6	-58.8	-49.2
1.5	-58.3	-58.0	-37.3
2.0	-58.3	-56.0	-25.6
3.0	-58.0	-51.3	-21.1
4.0	-57.3	-48.7	-16.0
5.0	-52	-29	-2.3
6.0	-45	-28	0

* Average of triplicate measurements .

** Immediately measured.

aSlope between 2.0 X 10-4 and 2.0 X 10-3 M TaF6-,

bSlope between 2.0 X 10-5 and 2.0 X 10-4 M TaF6-,

cSlope between 2.0 X 10-6 and 2.0 X 10-5 M TAF6-.

The decrease in the slope upon increasing sulphuric acid concentration might be due to the protonation of the membrane which possibly resulted in the dissolution of membrane, and the increasing degree of hydrolysis of tantalum(V) and its lower concentrations.

Eventhough the slope was found to be better without sulpuric acid the potential readings were not very stable. It should also be noted that the measurements at zero concentration of acid were made immediately to avoid hydrolysis of tantalum(V) in the test solution.

Thus, the optimum concentration range of sulphuric acid with a better slope and linear range was found to be 0.5 - 1.5 M. A 1.0 M sulphuric acid was, therefore, chosen for further study, since the linear range was also better, 2.0 X 10-6 - 1.0 X 10-2 M tantalum(V), (Fig.6). The average slope calculated, from the optimum concentration range, was to be -58.5 1.5 mV per decade.

4.4.2 Effect of Hdrofluoric Aclid Concentration. In this study, the concentration of sulphuric acid was kept constant at 1.0 M, and the concentration of hydrofluoric acid was varied between 0.1 and 5.0 M.

It was found that the potential increases with increasing concentration of hydrofluoric acid up to 0.5 M and then practically remained constant. This may be due to the decrease in the degree of dissociations in 1.0 m sulphuric acid.

The electrode responded with a sub-Nernstian slope upto 2.0 X 10-5 M tantalum(V) from 0.1 to 2.0 M hydrofluoric acid in the system. However, upon increasing the concentration of hydrofluoric acid above 2.0 M, the magnitude of the slope decreased at lower metal concentrations, i.e., below 2.0 X 10-5 M (Table 4).

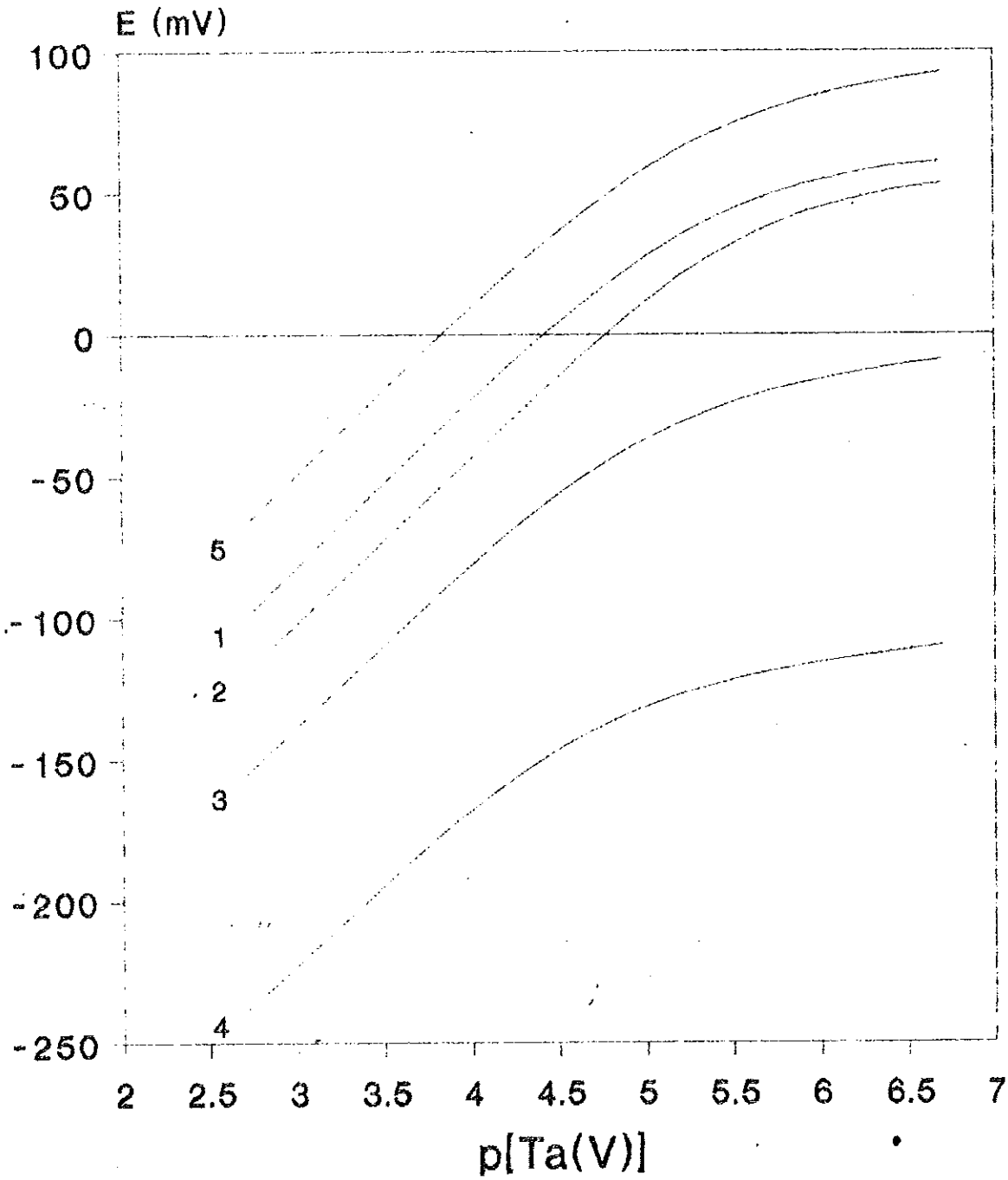

Fig.6. Effect of sulphuric acid concentration on the response behaviour of the electrode, (1) 0.0 M (2) 0.5 M (3) 1.0 M (4) 2.0 M (5) 4.0 M

Table 4. Effect of the concentration of hydrofluoric acid on the slope of the BG+TaF6- liquid membrane electrode*

[H2SO4] = 1.0 M

HF, M	Slopea mV/decade	Slopeb mV/decade	Slopec mV/decade
0.1	-59.5	-54.1	-40.5
0.5	-59.0	-58.9	-45.8
1.0	-59.0	-57.7	-51.3
1.5	-60.0	-57.9	-44.6
2.0	-60.5	-57.2	-35.7
3.0	-60.2	-57.9	-28.2
4.0	-59.7	-52.8	-24.9
5.0	-60.4	-49.8	-19.0

* Average of triplicate measurements.

aSlope between 2.0 X 10-4 and 2.0 X 10-3 M TaF6-,

bSlope between 2.0 X 10-5 and 2.0 X 10-4 M TaF6-,

cSlope between 2.0 X 10-6 and 2.0 X 10-5 M TaF6-.

Thus, the optimum concentration of hydrofluoric acid with a better linear range was found to be 0.5 - 1.5 M hydrofluoric acid. The average slope in the optimum concentration range was also found to be -58.5 $\pm$ 1.5 mV per decade. Therefore, a 1.0 M hydrofluoric acid concentration was chosen since a better linear range, 2.0 X 10-6 - 1.0 X 10-2 M tantalum(V), was obtained.

4.4.3 Effect of Ammonium Fluoride Concentration. In order to improve the linear range and to avoid the use of hydrofluoric acid, ammonium fluoride was used as the comlexing agent. The concentration of ammonium fluoride was varied from 0.1 M to 3.0 M keeping the concentration of sulphuric acid at 1.0 M.

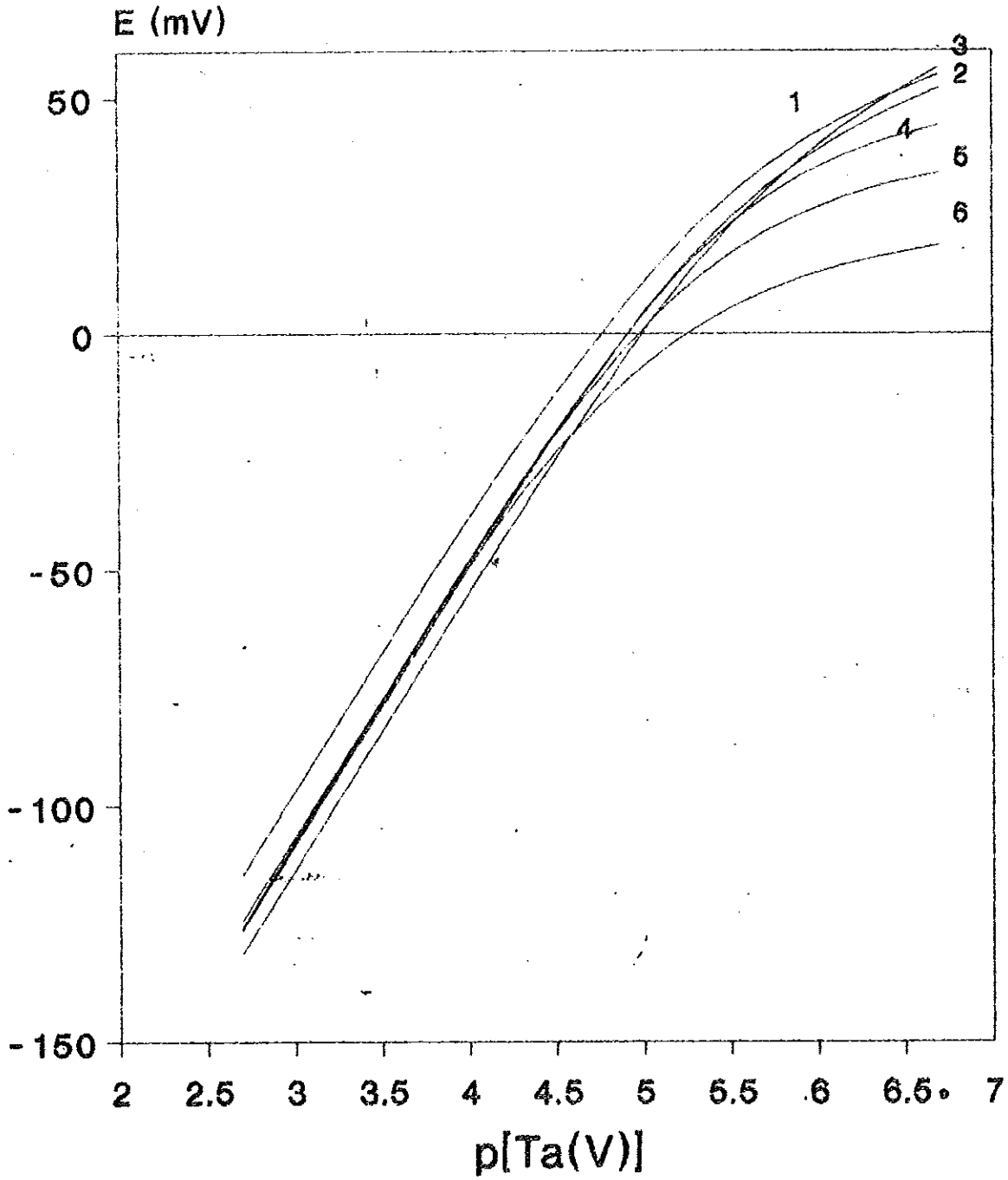

Fig.7. Effect of hydrofluoric acid concentration on the response behaviour of the electrode, (1) 0.1 M (2) 0.5 M (3) 1.0 M (4) 1.5 M (5) 2.0 M (6) 4.0 M

The potential was found to decrease when the concentration of ammonium fluoride exceeded 0.5 M. This phenomenon can probably be due to the formation of higher comlexes (TaF_7^{2-}) together with TaF_6^-. Consequently, the magnitude of the slope decreased in the lower concentrations of tantalum(V). The optimum concentration range of ammonium fluoride with a better slope and lilnear response range was found to be 0.5 - 1.0 M (Table 5).

The response behavior of the electrode, in 0.5 M ammonium fluoride and 1.0 M sulphuric acid was studied in detail, and the calibration curve is shown in Fig. 8. The linear range was found to be 3.55 X 10-6 - 1.0 X 10-2 M tantalum(V) with an average slope in the optimum concentration range and detction limit of -55.7 ± 2 mV per decade and 7.76 X 10-7 M tantalum(V), respectively.

Table 5. Effect of ammonium fluoride concentration on the slope of the BG+TaF_6^- liquid membrane electrode*

[H_2SO_4] = 1.0 M

NH_4F, M	Slopea mV/decade	Slopeb mV/decade	Slopec mV/decade
0.1	-55.5	-56.8	-37.8
0.5	-61.1	-57.5	-41.6
1.0	-61.0	-53.9	-35.3
1.5	-61.0	-49.1	-18.5
2.0	-56.1	-31.5	-7.1
3.0	-31.3	-3.4	-3.5

* Average of triplicate mesurements.

aSlope between 2.0 X 10-4 and 2.0 X 10-3 M TaF_6^-,

bSlope between 2.0 X 10-5 and 2.0 X 10-4 M TaF_6^-,

cSlope between 2.0 X 10-6 and 2.0 X 10-5 M TaF_6^-.

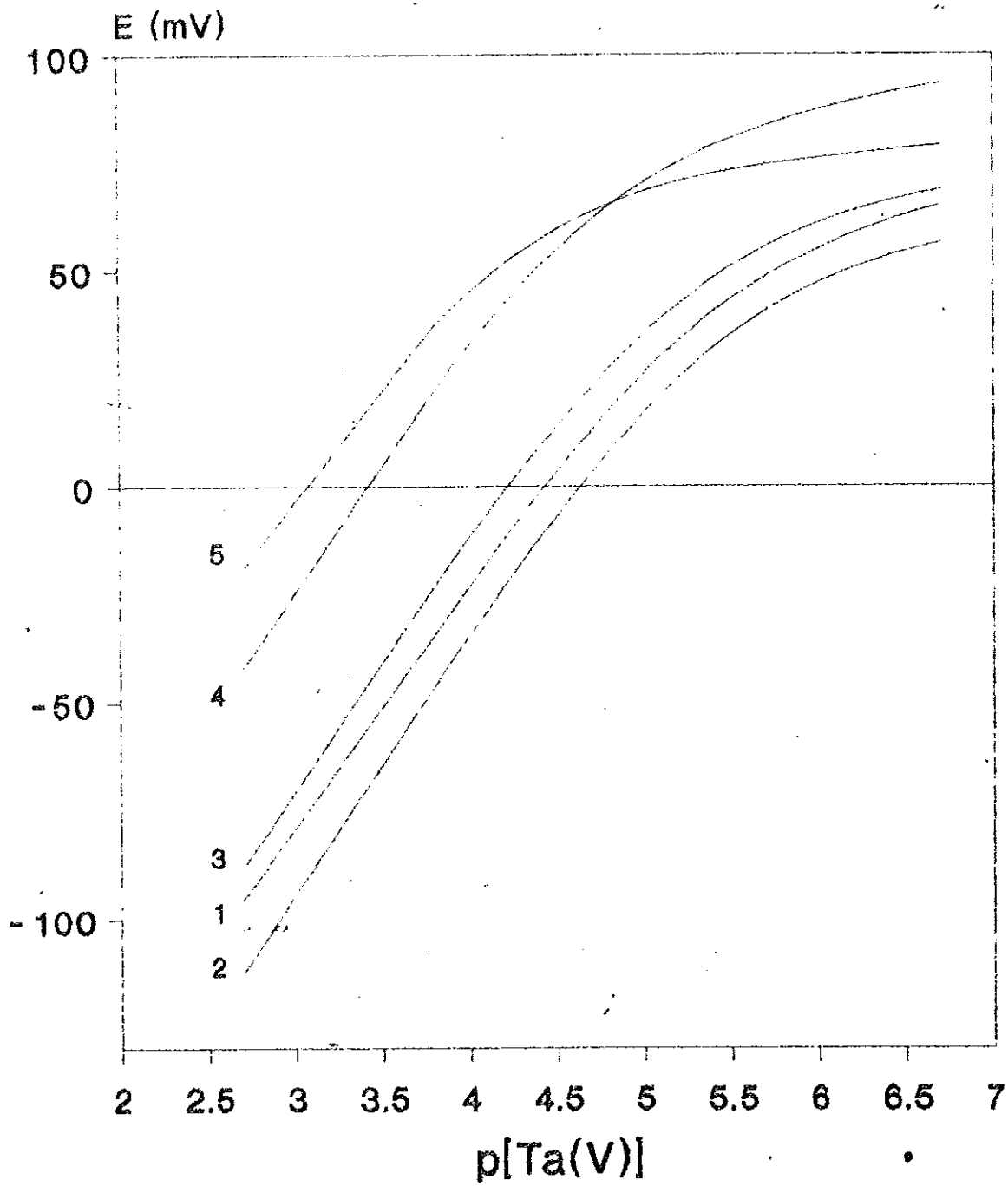

Fig.8. Effect of ammonium fluoride concentration on the response behaviour of the electrode, (1) 0.1 M (2) 0.5 M (3) 1.0 M (4) 1.5 M (5) 2.0 M

The $BG^{+}TaF_{6}^{-}$ liquid membrane electrode was found to respond to TaF_{6}^{-} ions. The response behavior of the electrode was studied in the concentration of 1.0×10^{-7} - 1.0×10^{-2} M tantalum(V) that were 1.0 M in both sulphuric and hydrofluoric acid. However, the electrode responded linearly in the concentration range of 2.0×10^{-6} - 1.0×10^{-2} M tantalum(V) with a sub-Nernstian slop of -58.5 ± 1.5 mV per decade.

The detection limit as defined by IUPAC was found to be 3.69×10^{-7} M tantalum(V). The response time was found to be 20-30 seconds for concentrations greater than 1.0×10^{-4} M tantalum(V) and 30-120 seconds for lower concentrations.

The electrode was found to give a constant slope during its whole life. It was also found that the electrode responded properly over more than two months. The longer age of the electrode may probably be due to the diffusion of more ion exchanger from the reservior to the surface of the membrane to replace that which has dissoloved, if any. Similarly, a fresh membrane surface is always produced since it was rinsed and wiped out with tissue paper or cotton wool after each measurements to remove any contamination. Thus the life time of the electrode is dependent mainly on the serviceable life of the membrane support. This happens because the support becomes deformed or clogged with sample debris, allowing, respectively, leakage of the active material or impedance of the replenishment, causing electrode mulfunction.

The potential drift of not more than 2 mV was noted during 24 h. This was carried out by measuring the potentials of two known and constant concentrations of the determinand at least twice a day.

All measurements were carried out at an ambient temperature (20 ± 2^{0}C). The response curve was obtained by plotting the measured potential (E, mV) vs. - log C_i (Fig.9).

The optimum conditions and response characteristics of the Brilliant Green-hexafluorotantalate(V) liquid membrane electrode are summarized in Table 6.

Table 6. Optimum conditions and response characteristics $BG^{+}TaF_6^{-}$ liquid membrane electrode

Parameter	Optimum condition/value
Membrane solvent	Nitrobenzene
Exchanger concentration, M	5.0×10^{-3}
Saturation time, h	36
H_2SO_4 concentration in the test solution, M	1.0
HF concentration in the test solution, M	1.0
Linear range, Ta(V) concentration, M	2.0×10^{-6} - 1.0×10^{-2}
Slop, mV/decade	58.5 ± 1.5
Detection limit, Ta(V) concentration, M	3.69×10^{-7}
Response time, seconds	20-120
Presision, RSD, (n=6)	2.56%

4.6 Interference Studies

The effects of several diverse ions on the response of the Brilliant Green-hexafluorotantalate(V) liquid membrane electrode to hexafluorotantalate(V)

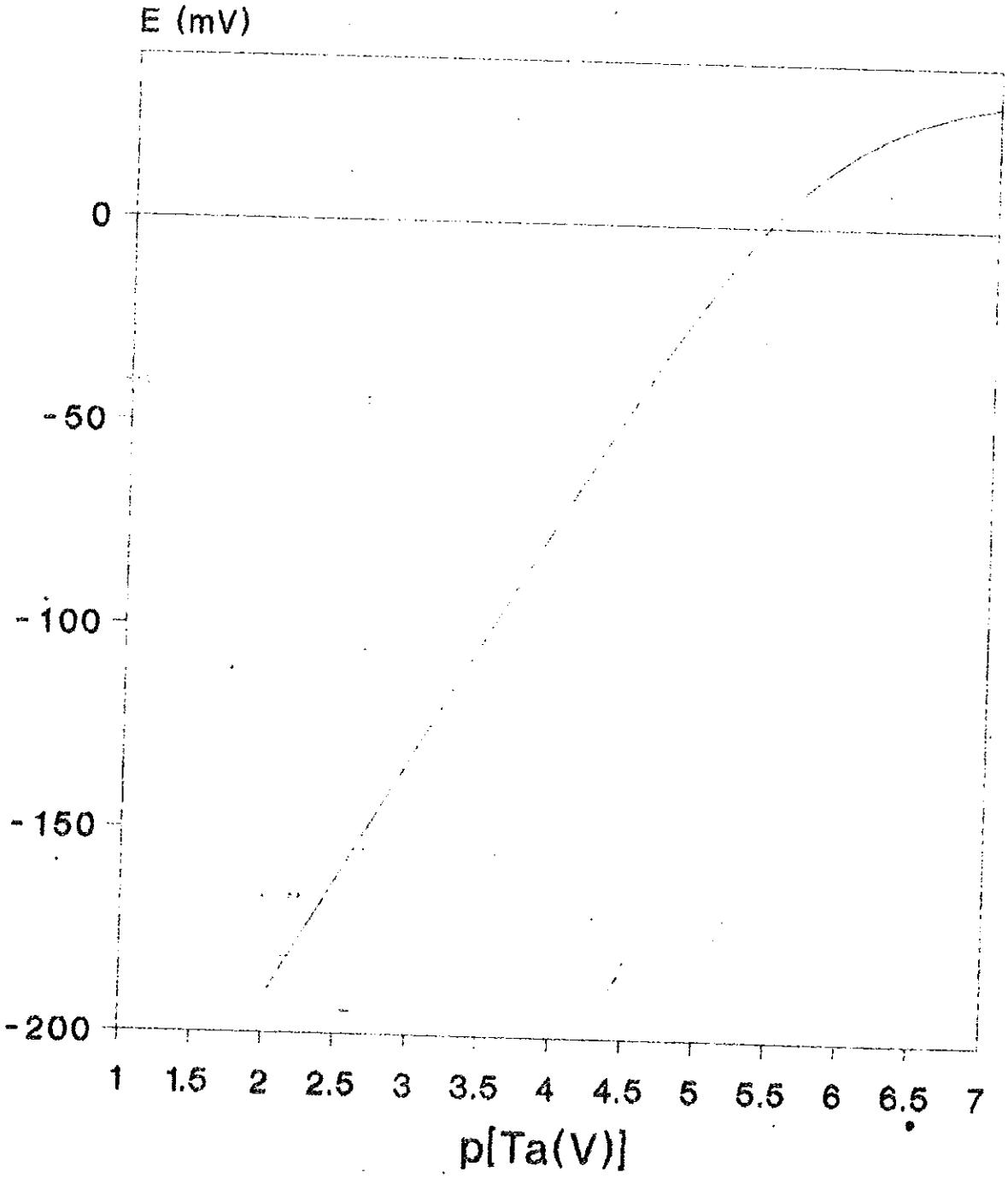

Fig. 9 Calibration curve for determination of tantalum(V)

ion have been studied to evaluate the selectivity coefficient, K_{ij}^{pot}, Both the separate and mixed solution methods were employed to calculate the selectivity coefficient values using equations (2.31) and (2.32), respectively. In mixed solution method equation (2.32), togerther with the calibration curves (section 2.3), were used to evaluate K_{ij}^{pot}.

The selectivity coefficients, K_{ij}^{pot}, have been calculated for several anions and some metal ions which form anionic fluoro-complexes in 1.0 M sulphuric acid and 1.0 M hydrofluoric acid solutions. The results are given in Table 7.

The values of K_{ij}^{pot} obtained by the separate and mixed solution methods were not the same probably because of the difference in the experimental conditions such as mechanism of the electrode response and changing environment of the ions in solution[78]. It can be noted that K_{ij}^{pot} values obtained by the two methods are not necessarily the same as reported for the other liquid membrane electrodes[79].

No serious interference was noted from NO_3^-, Cl^-, SO_4^-, $C_2O_4^{2-}$ and EDTA ions on the response behavior of the electrode to hexafluorotantalate(V) in both the separate as well as the mixed solution methods. There was also no serious interference due to Mn^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+}. This might be due to the greater tendency of these cations to form the sulphates in sulphuric acid solutions[80]. The sulphates of these cations are more stable than their fluorides and fluoro-complexes.

Fe^{3+} and Al^{3+} ions tend to form hexafluorocomplexes[81], but strong interference was not noted in the presence of these tarvalent complexes. The presence of Zr^{4+}, Sb^{3+} and As^{3+} did not interfere seriously. These cations mainly have a strong affinity to form compounds with sulphates[80,82]

Table 7. Selectivity coefficients, K_{ij}^{pot}, of Brilliant Green-hexafluorotantalate(V) liquid membrane electrode

Interfering ion	Most probable fluoro-complexes in 1.0 M H_2SO & HF	Refer-nces	K_{ij}^{pot}	
			Separate solution method	Mied solution method
ClO_4^-	-	-	$1.76X10^{-2}$	$1.00X10^{-2}$
SCN^-	-	--	$5.07X10^{-3}$	$1.49X10^{-2}$
IO_4^-	-	-	$2.28X10^{-3}$	$3.54X10^{-3}$
W^{6+}	WF_8^{2-}	131	$1.32X10^{-3}$	$.84X10^{-5}$
Cr^{3+}	$CrF_5H_2O^{2-}$	131	$9.84X10^{-5}$	$1.33X10^{-4}$
Ti^{4+}	TiF_6^{2-}	80	$3.76X10^{-5}$	$7.93X10^{-5}$
Ag^+	AgF_3^{2-}	80	$3.61X10^{-5}$	$7.84X10^{-5}$
Cu^{2+}	CuF_4^{2-}	80	$4.89X10^{-5}$	$6.68X10^{-5}$
Cd^{2+}	CdF_4^{2-}	80	$5.03X10^{-5}$	$8.40X10^{-5}$
UO_2^{2+}	$UO_2F_4^{2-}$	81	$5.61X10^{-5}$	$1.99X10^{-5}$
Fe^{3+}	FeF_6^{3-}	81	$2.63X10^{-5}$	$2.97X10^{-5}$
Al^{3+}	AlF_6^{3-}	81	$1.08X10^{-5}$	$2.47X10^{-5}$
Bi^{3+}	BiF_4^-	82	$1.72X10^{-5}$	$2.65X10^{-3}$
Pb^{2+}	PbF_4^{2-}	82	$5.83X10^{-5}$	$3.98X10^{-5}$
Sn^{2+}	SnF_4^{2-}	82	$3.74X10^{-5}$	$7.07X10^{-5}$
Nb^{5+}	$NbOF_5^{2-}$	24	$4.01X10^{-5}$	$8.23X10^{-4}$
Ca^{2+}	CaF_4^{2-}	83	$8.09X10^{-5}$	$1.59X10^{-4}$
Boric acid	BF_4^-	83	$4.51X10^{-5}$	$9.98X10^{-3}$
Fluoroboric acid	BF_4^-	83	$5.97X10^{-3}$	$1.58X10^{-3}$

There is no information on fluoro-complex formation with Y^{3+} and La^{3+} ions[80]. However, the presence of these ions in the solution showed mild interference for some unknown reason. Though the formation of fluoro-complex was reported for Hg^{2+} there is no structural information[80]. However, the presence of Hg^{2+} did not impart any interference.

In both separate and mixed solution methods Er^{3+} and Ce^{4+} ions formed precipitate upon addition of hydrofluoric acid. However, formation of these precipitates did not affect the stability of the potential readings and their presence did not interfere on the response of the electrode to hexafluorotantalate(V) anion.

No interference was noted in the presence of VO_3^- by both methods. This is probably because it undergoes polumerization reactions[80].

The study of the effect of niobium is of special concern. Niobium, which also form the oxyfluoro-complex[24], $NbOF_5^{2-}$, in 1.0 M sulphuric acid and 1.0 M hydrodluoric acid, showed mild interference on the response characteristics of the electrode.

Several cations such as Bi^{3+}, Pb^{2+}, Sn^{2+}, UO_2^{2+}, W^{6+}, Cr^{3+}, Ti^{4+}, Ab^{+}, Cu^{2+}, Cd^{2+} and Ca^{2+} form fluoro-complexes of various compositions . However the calculation of the selectivity coefficients is based on the very frequently occuring fluoro-complexes (Table 7). These results indicate that these ions do not cause strong interference on the response of Brilliant Green-hexafluorotantalate(V) liquid membrane electrode to TaF_6^-.

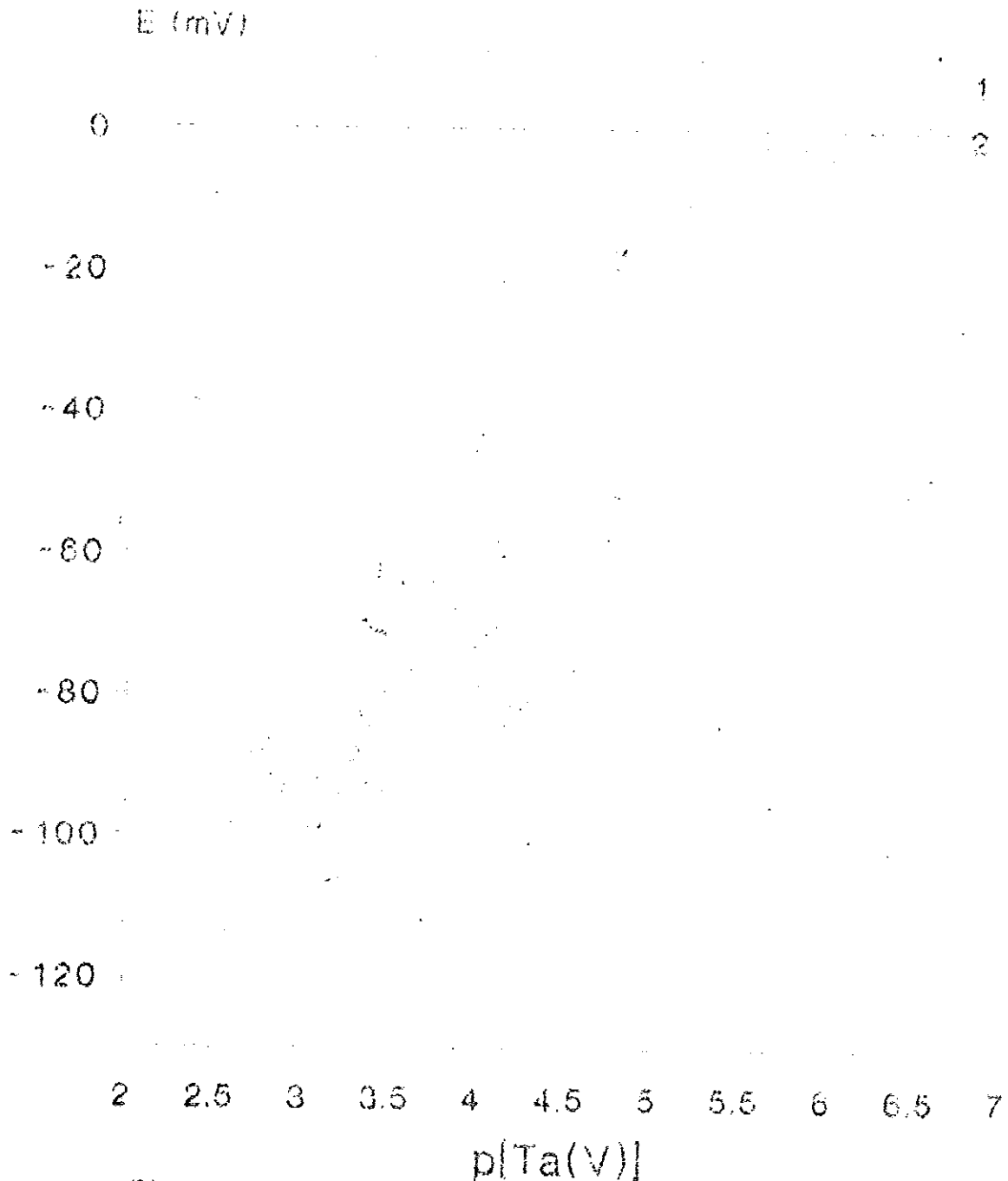

Fig.11. Response curves of the electrode in the presence of, (1) boric acid and (2) fluoroboric acid

4.7 Application of the Brilliant Green-hexafluorotantalate(V) liquid Membrane Electrode

The Brilliant Green-hexafluorotantalate(V) liquid membrane electrode was applied to the quantification of tantalum in the real and artificial samples.

The reliablity of the fusion method, used for sample preparation, and of the proposed liquid membrane electrode was first assessed by determining the tantalum content of an artificial sample of similar composition to that of a real ore. The sample was prepared by mixing the required quantity of Ta_2O_5, Nb_2O_5, $Fe(NO_3)_3\ 9H_2O$ and $MnSO_4 6H_2O$, and the sample solution was prepared by procedure described in section 3.2.3. The tantalum content of the sample solution was determined by the proposed electrode using four different measurement techniques; viz, direct potentiometry, standard addition, sample addition and Gran's plot. The results obtained (Table 9 and Fig. 12 for Gran's plot) are in good a agreement with the actual values.

The reliability of the proposed liquid membrane electrode was further assessed by determining the tantalum content of two Ethiopian tantalite-columbite ore samples (which were collected from Ethiopian Institute of Geological Surveys) using four different potentiometric measurement techniques, mentioned above. The results are summarized in Table 10 and 11, and Fig. 13 and 14.

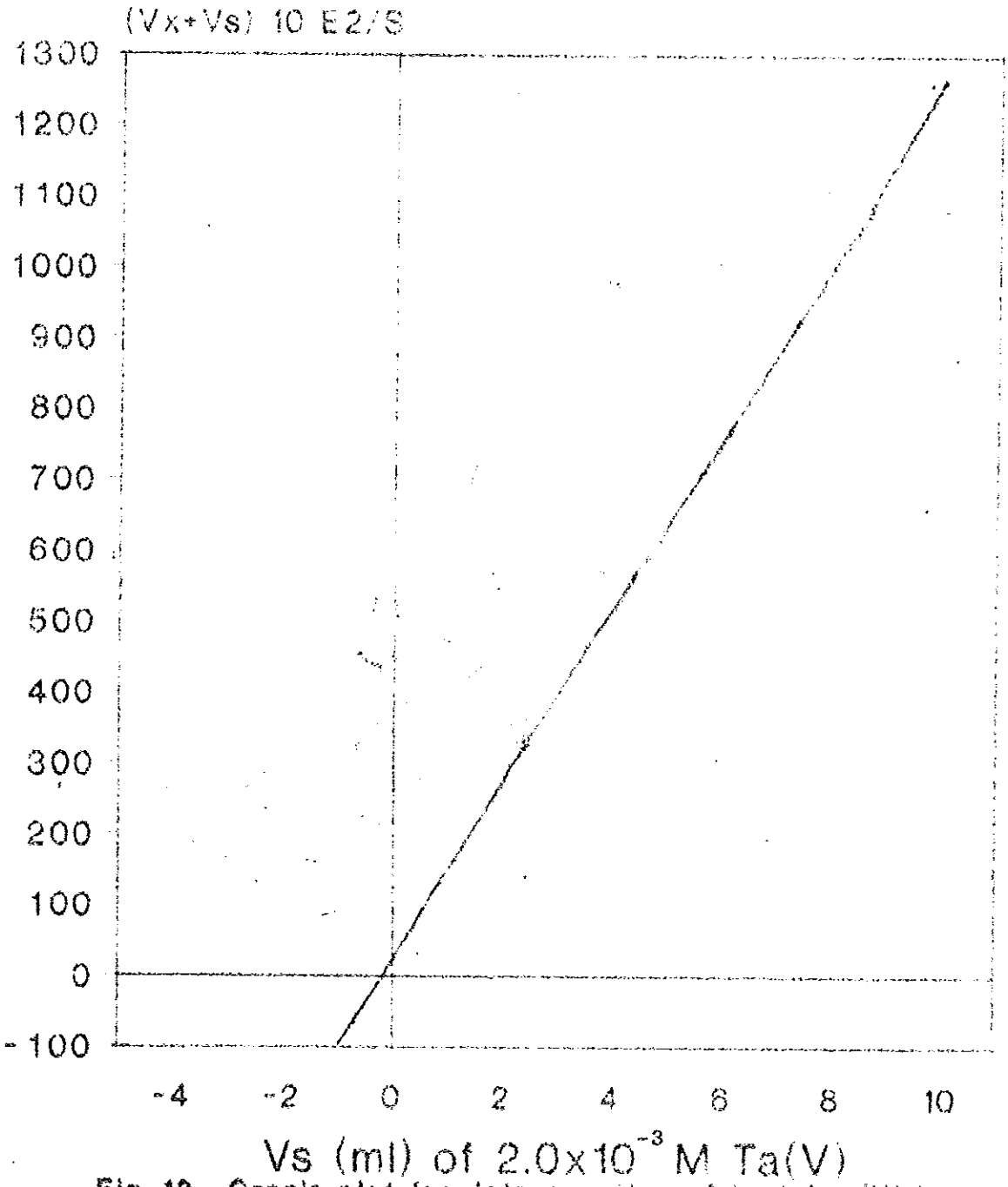

Fig. 12. Gran's plot for determination of tantalum(V) in artificial sample by multiple standard addition

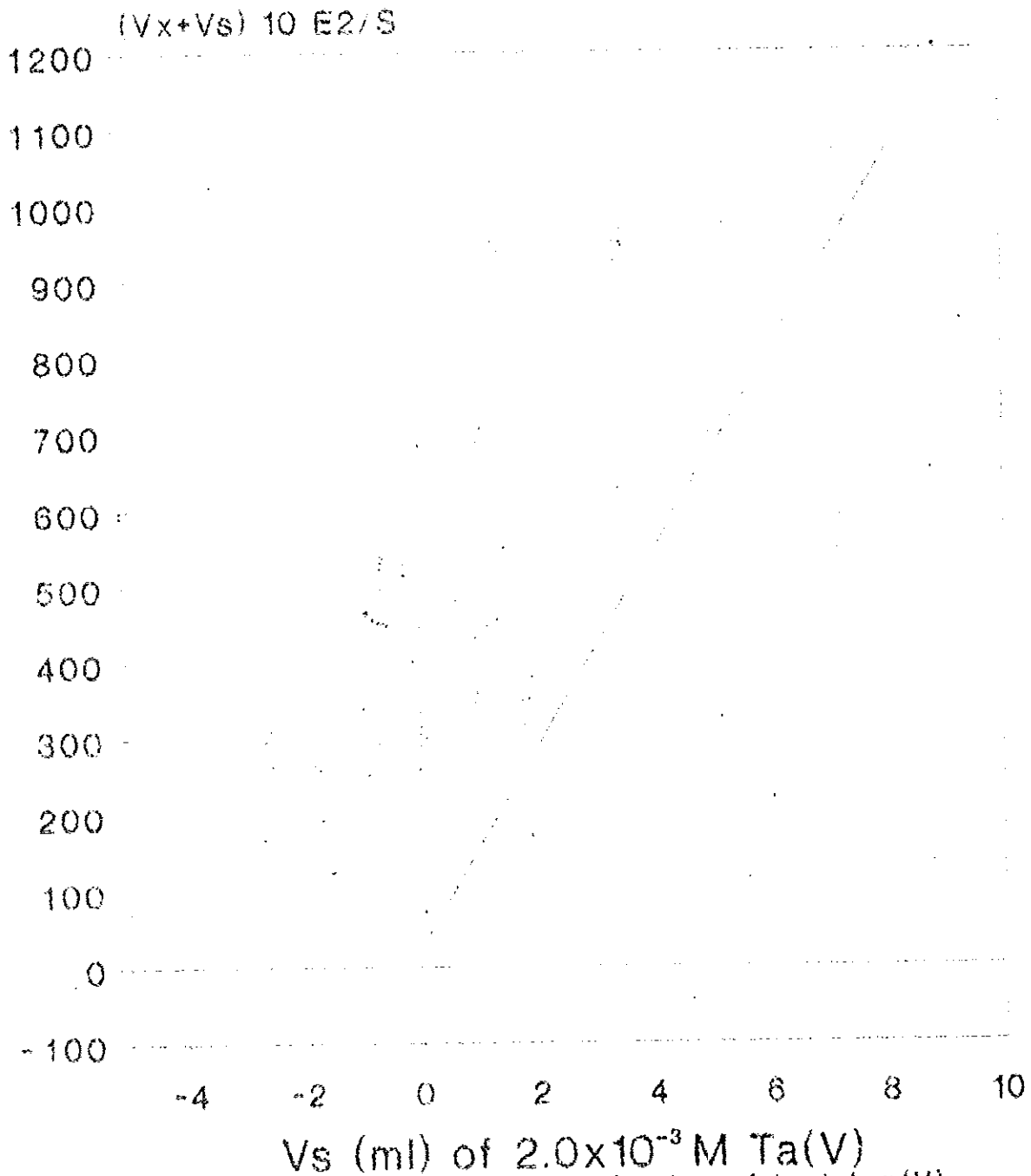

Fig. 13. Grant's plot for the determination of tantalum(V) in Ethiopian tantalite-columbite ore (sample No.334101).

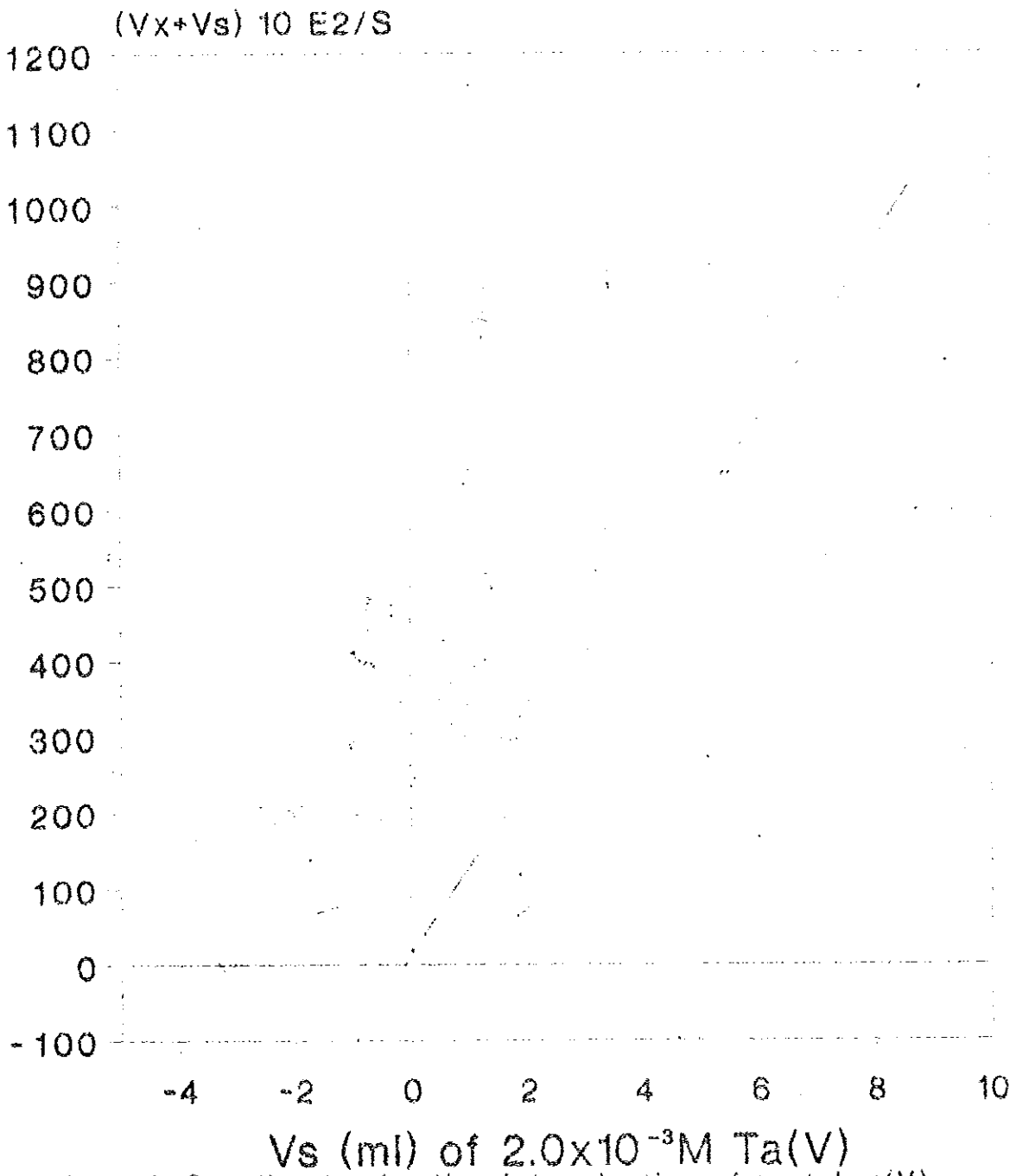

Fig. 14. Grant's plot for the determination of tantalum(V) in Ethiopian tantalite-columbite ore (sample No.334107).

Thus the Brilliant Green-hexafluorotantalate(V) liquid membrane electrode can be applied to determine tantalum in diverse samples with reasonable precision and accuracy.

Table 9. Analysis of tantalite-columbite artifical ore sample (Ta_2O_5, 65.5%; Nb_2O_5, 31.0%; $Fe(NO_3)_3.9H_2O$, 1.8%; and $MnSO_4.H_2O$, 1.7%)

Method	Ta_2O_5 found* percent	Equation No. used for calculation
Direct potentiometry	65.48 ± 0.41	2.22
Standard addition	66.13 ± 0.82	2.27
Sample addition	64.83 ± 0.74	2.31
Gran's plot	65.22 ± 0.39	2.32

* Mean ± 95% confidence limits for triplicate measurements.

Table 10. Analysis of Ethiopian tantalite-columbite ore sample, No. 334101 (Ta_2O_5 certified by EIGS was 65.5%)

Method	Ta_2O_5 found* percent	Equation No. used for calculation
Direct potentiometry	64.89 ± 0.93	2.22
Standard addition	64.75 ± 1.07	2.27
Sample addition	63.92 ± 1.34	2.31
Gran's plot	66.20 ± 0.46	2.32

* Mean ± 95% confidence limit for triplicate measurements.

Table 11. Analysis of Ethiopian tantalite-columbite ore sample, EIGS sample No. 334107 (Ta_2O_5 certified by EIGS was 49.5%)

Method	Ta_2O_5 found*, percent	Equation No. used for calculation
Direct potentiometry	48.27 ± 1.75	2.22
Standard addition	49.52 ± 0.43	2.27
Sample addition	48.16 ± 1.54	2.31
Gran's plot	50.07 ± 0.67	2.32

* Means ± 95% confidence limit for triplicate measurements.

4.8 Comparison with other Hexafluorotantalate(V)-selective Electrodes

An attempt was made to compare the response characteristics of the proposed liquid membrane electrode with other hexafluorotantalate(V)-selective electrodes. The reported data are summarized in Table 12.

65. M. Qureshi, H. S. Rathore and J.S. Thakur, Talanta, 25, 323 (1978).

66. R.D. Maslennikova and A.S. Chernyak, J. Org. Chem. (USSR), 13, 642 (1968).

67. Z. Shen and R. Xu, Huaxue Xuebao, 46, 69 (1988); Anal. Abstr. 50, 7B113 (1988).

68. A. Sanz-Medal, C.C. Rica and J.A. Perez-Bustamante, Anal. Chem., 52, 1035 (1980).

69. T. Wondimu, M.Sc. Thesis, AAU, 1989.

70. G. Moges, B.S. Chandravanshi and T. Bekele, Bull. Chem. Soc. Ethiop., 2, 1 (1988).

71. G.A. Rechnitz, M.R. Kresz and J.B. Zamochnik, Anal. Chem., 38, 973 (1966).

72. R.A. Drust, Mikochim, Acta, 3, 611 (1969).

73. B. Karlberg, Anal. Chem., 43, 1911 (1971).

74. S. L. Burden and D.E. Euler, Anal. Chem. 47, 793 (1975).

75. W. E. Mort, D. Amman, E. Pretsch and W. Simon, Pure Appl. Chem., 36, 421 (1973); Chem. Abstr., 79, 111158h (1973).

76. H.R. Wuhrmann, W.E. Mort and W. Simon, Helv. Chim. Acta, 56, 1011 (1973).

77. J.A. Riddik, W.B. Bunger, "Organic Solvents, Physical Properties and Methods of Purification", in Techniques of Chemistry, Vol. 2, 3rd ed. Wiley Interscience, New York, 1970.

78. Pure Appl. Chem. 129 (1976).

79. C. Liteanu, E. Hopiratean, C. Popescu, I. Rica and Stefaniga, Anal. Chem., 50, 1202 (1978).

80. "Comprhensive Inorganic Chemistry", Vol. 3, Eds. J.C. Bailor, H.J. Emeleus, R. Nyholm and A.F. Trotman-Dickenson, Pergamon Press, Oxford, 1973.

81. J. Inczedy, "Analytical Applications of Complex Equilibria", Ellis Horwood, Chichester, 1976.

82. "Comprhensive Inorganic Chemistry", Vol. 2, Eds. J.C. Bailor, H.J. Emeleus, R. Nyhlom and A.F. Trotman-Dickenson, Pergamon, Oxford, 1973.

83. "Comprhensive Inorganic Chemistry", Vol. 1, Eds. J.C. Bailor, H.J. Emeleus, R. Nyholm and A.F. Trotman-Dickenson, Pergamon, Oxford, 1973.